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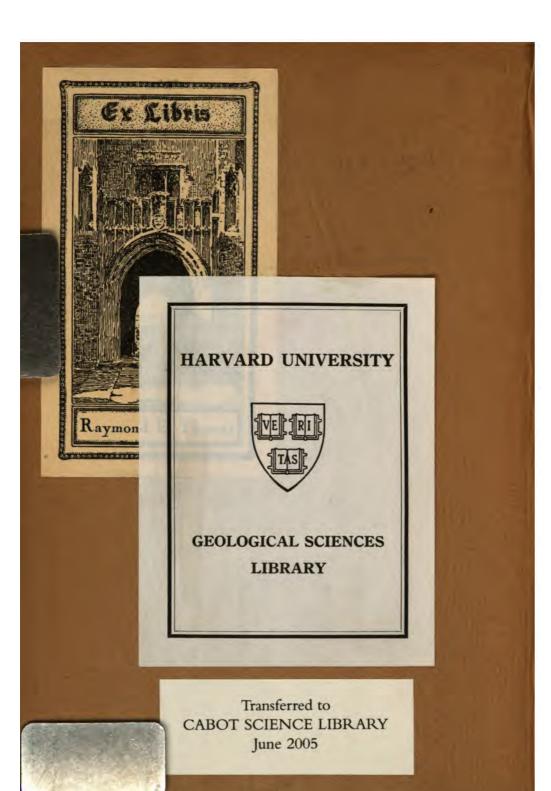
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H. J.

TO WHOSE INSPIRATION
MY INTEREST IN METALLOGRAPHY IS DUE

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PREFACE

This little book has been written to meet the needs of those students of General Science on Engineering who do not specialize in Metallography but who will use it to a limited extent in connection with their professional work.

It is hoped that it will be of service, also, to the general reader as an introduction to an increasingly important branch of service and as an aid to the better understanding of the more highly specialized books.

Greater emphasis has been laid on the applications of Metallography than on the physico-chemical principles involved but it is believed that the fundamental ideas on which metallography is based have not been neglected.

In the appendix will be found a few of the tables most commonly used by the metallographist, a suggested outline of a brief laboratory course and a descriptive list of the more important books and journals dealing with the subject.

Thanks are due to the authors of many of the standard books on metallography which have been freely used in the preparation of this little volume and grateful acknowledgment is made for the use of a few drawings which have been copied with minor changes from other books.

Special thanks are due to Messrs. Bauer and Deiss from whose book on "The Sampling and Chemical Analysis of Iron and Steel" most of the microphotographs of steel and iron have been taken.

It is a pleasure to express my appreciation for the services of Professor L. F. Hamilton who has helped greatly by his kindly criticism of the proof.

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PRINCIPLES OF METALLOGRAPHY

CHAPTER I

THE SIMPLE ALLOY DIAGRAM

An alloy may be defined as the solid which results when two or more metals harden from the molten state. In a few rare cases alloys are prepared in other ways as, for instance, by compression of the solid metals or by electrolytic deposition, but the amount of material alloyed in this way is negligible.

Metallography, or Physical Metallurgy as it is sometimes called, is the general study of metals and alloys. In its more restricted sense it deals with finished alloys, their physical and chemical properties, their internal structure, the methods of investigation and, perhaps most important of all, the study of the mechanical properties and defects of the commercial alloys.

When a pure metal is melted under conditions which make it possible to determine the changes of temperature during the cooling and these changes are indicated in graphical form, a curve of the following form is obtained (Fig. 1). The temperature readings are taken at definite time intervals and in plotting the curve these temperatures are used as ordinates while the corresponding time intervals are abscissæ. The solidification of lead has been selected as an example, with time intervals of ten seconds. It will be noticed that the curve

falls smoothly until the temperature of 327°C. is reached when it breaks sharply and remains horizontal indicating a constant temperature during an appreciable period. The curve again falls gradually to ordinary temperatures without further abrupt changes in direction. The horizontal line represents the transition of the lead from the liquid to the solid state. The heat which is necessary to maintain the mass at constant

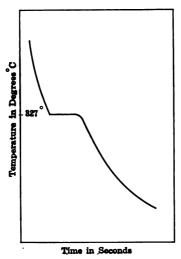


Fig. 1.—Cooling curve of pure lead.

temperature is the latent heat of solidification. Since the amount of heat liberated at this time is proportional to the mass of metal solidifying, it is evident that, other conditions being equal, the length of the horizontal is a measure of the amount of material present. This does not hold absolutely in practice as it is impossible to get ideal cooling conditions but it is true to such a degree of approximation that the fact is of great value in the thermal study of alloys. The horizontal has the additional physical significance that it indicates the only temperature at which solid and molten lead will stay in contact with each other indefinitely. At any higher temperature solid lead will disappear and at a lower one there will be no liquid. Several other methods of drawing these "cooling curves" will be described later in connection with the laboratory study of the alloys.

The Two Layer Alloy.—The simplest possible alloy is one which results from the solidification of two metals

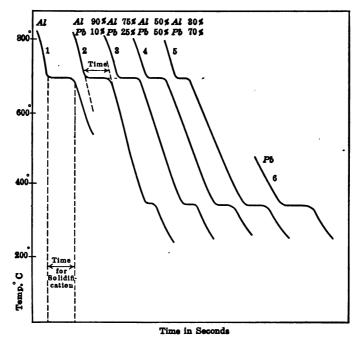


Fig. 2.—Cooling curves of aluminum, lead and four alloys.

which do not mix even when they are in the molten condition. In the strictest sense this is probably not a true alloy but the subject deserves consideration because of the practical application of certain of these non-miscible metal pairs in the form of solid emulsions. If aluminum and lead are mixed in varying proportions, the mixtures melted, allowed to cool under conditions as

nearly identical as possible and temperature readings are taken at definite time intervals during the cooling, a series of curves like that shown in Fig. 2 will be obtained. Curve No. 1 is the cooling curve of pure aluminum and each successive curve represents the cooling of an alloy containing more lead than the one before it until pure lead solidifies as indicated in Curve No. 6.

This method of representing the temperature changes in a series of alloys is not satisfactory even in so simple a case and it becomes impossible in more complicated This has lead to the use of a graphical form of representation known sometimes as the "freezing point diagram" but, more accurately, as the equilibrium diagram of the alloys. Disregarding for a moment the time taken for each alloy to solidify, as shown by the horizontal lines in the series of curves, it is evident that the temperature changes may all be indicated on a chart in which the ordinates represent temperatures and the abscissæ percentage composition of the different alloys. Since, in the case under consideration, the melting point of neither metal is affected by the presence of the other, the freezing point diagram consists of two horizontal lines only, one at the melting point of aluminum, the other at the melting point of lead.

In his various papers on Thermic Analysis, Tammann¹ has shown that, in addition to the simple freezing point diagram given above, the introduction of a curve, or curves, showing the time interval during which the temperature stays constant for each alloy of a series is exceedingly valuable both in the construction and in the interpretation of these equilibrium diagrams. The time curves are obtained and applied to the diagram as follows: a straight edge is applied to the sloping parts of each cooling curve as shown in Curve No. 2, Fig. 2

¹ Zt. Anorg. Chem., 37 (1903), 303; 45 (1905), 205; 47 (1906), 289.

and the resulting sloping lines are connected by horizontal lines drawn through the horizontal parts of the cooling curves. The distance between the points of intersection of each horizontal line with the two oblique lines which it crosses represents the time either of solidification or of some other change taking place at constant temperature. In Tammann's earlier work these time lines were drawn from the horizontal temperature lines to which they referred as shown in Fig. 3. This led to

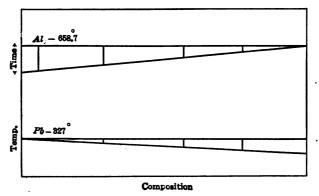


Fig. 3.—Aluminum-lead diagram.

a certain amount of confusion as one set of ordinates had to be used to indicate both time and temperature. In the more recent work of other metallographists the time curves are made a separate part of the diagram as shown in Fig. 4.

Since, as was stated on p. 2, the time taken for a metal to solidify is proportional to the amount of material present when the cooling conditions are substantially identical, it is obvious that the time of solidification of the aluminum will be greatest where its amount is greatest and will decrease to zero where only lead is present. The triangle which is formed by drawing a line through the ends of the time perpendiculars is

useful in several ways. From it may be determined not only how much time will be required for any alloy in the series to solidify, no matter what its composition, but also, what is far more important, the percentage composition of the alloy. It is only necessary to cool an equal weight of the unknown specimen under standard conditions, determine the time interval on its cooling curve and locate the same time interval on the equi-

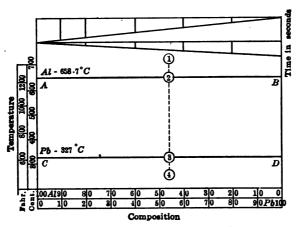


Fig. 4.—Aluminum-lead alloys (GROYER). The ordinates of the triangles marked "time in seconds" correspond to the horizontal lines in the curves of Fig. 2.

librium diagram. The point at which the ordinate of the time triangle has the same length as the unknown time interval indicates the percentage composition of the alloy. This is the fundamental idea of Thermic Analysis and, while the results do not compare in accuracy with ordinary quantitative methods nor can the method be used at all in many cases, it is quite possible, in those instances in which it may be used, to get results very rapidly indeed and with a degree of accuracy which is often sufficiently great for much commercial alloy work.

The complete equilibrium diagram makes it possible

to predict the physical condition of any alloy in the series at any temperature included in the diagram. question of the interpretation of diagrams is one of the greatest importance to the metallographist. as an example the behavior of an unknown alloy x, Fig. 4, during its cooling from a temperature 1 to the temperature 4. Since the diagram shows that in all mixtures of this series the first heat evolution occurs at the temperature of the line AB it follows that all alloys above that line and, therefore, alloy x will be in the liquid condition at the temperature 1. When the temperature has fallen to that indicated by AB, or point 2 on the dotted line, a temperature effect is noticed on the diagram. Since this evolution of heat takes place at the same temperature for all alloys of the series and since it corresponds to the melting point of aluminum, the assumption is justified that at and below the point 2 the mass consists of crystals of aluminum suspended That this assumption is in a mass of fused material. correct may be shown by removing some of the solid material at any temperature lower than that of point 2 and higher than point 3. It will be found to be pure aluminum. At point 3 on the line CD a second heat effect is shown and since this point corresponds to the melting point of lead the same line of reasoning as before shows that this effect represents the solidification of the lead which the mixture contained. As no further heat changes are shown on the diagram it may be assumed that alloy 4 is a solid mixture of aluminum and lead.

The diagram as drawn gives the following general information with regard to alloys of aluminum and lead. At any temperature above that represented by AB, any alloy of aluminum and lead, no matter what its percentage composition, will consist of a mixture of molten

aluminum and molten lead and in this particular case owing to the great difference in the specific gravity of the two substances it will consist of two distinct liquid layers. In the area between AB and CD all alloys consist of a mixture of solid aluminum and molten lead, the relative amounts of the two metals varying with the percentage composition. In the temperature range below CD the alloy is made up of solid lead and solid aluminum. Unless the alloy is vigorously stirred during the solidification, the solid will be found to consist of two distinctly separated layers.

After the construction of the diagram, or frequently in practice simultaneously with its construction, a microscopic study of the solid alloys is made. A highly polished surface free from scratches is obtained on which the internal structure of the alloy is brought out by treatment with suitable etching reagents which attack one constituent more than the other and produce in this way depressions in the surface, color changes of the constituent attacked or other differences which are noticeable under the microscope. The method of polishing the specimens and preparing them for microscopic examination will be considered in the section on Laboratory Methods, p. 18. The following microphotograph (Fig. 5) of a lead-aluminum alloy shows the way in which the microscope is used to confirm the results obtained by temperature measurements. As was to be expected from the diagram the microscope shows two distinct layers, the dark lead at the bottom and the lighter colored aluminum above it.

Plastic Bronze.—The most important example of the alloys formed by non-miscible metals is the class of copper-lead alloys known as plastic bronzes, much used as bearing metals. Melted lead forms an emulsion with melted copper and if the cooling of the alloy takes place

rapidly enough the lead will be found more or less uniformly distributed throughout the mass of copper in the form of spherical drops. By the addition of nickel or other high melting material in small amounts it is possible to prepare an alloy containing 50 per cent. lead though the usual plastic bronzes contain only from 15 to 30 per cent. lead. In alloys of this type the copper gives the necessary strength while the lead increases the plasticity of the alloy and acts as a lubricant.



Fig. 5.—Aluminum-lead alloy $(75 \times)$.

While it is probably true that no two metals are absolutely insoluble in each other, either in the liquid or in the solid state, the solubility in the case just described is so slight that for practical purposes it may be disregarded. There are many alloys of this class but those of copper and lead are the only ones of technical interest.

The Eutectic Alloy.—The next type of alloy to be considered is that in which the two metals are completely miscible in the liquid state and completely non-miscible, or insoluble in each other, in the solid state. It is a

well-known fact that in most cases in which one substance is added to another, in which it will dissolve, the freezing point of the solvent is lowered. An illustration of this phenomenon is the preparation of the ice-salt freezing mixture which is able to produce a temperature twenty-one degrees below that of ice alone. Numerous alloys behave in the same way. One of the best known of these is the lead-antimony alloy which has many important commercial uses. If a small amount of lead is added to molten antimony the freezing point

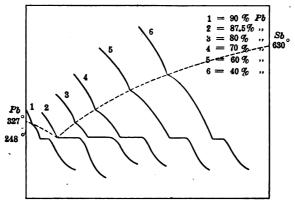
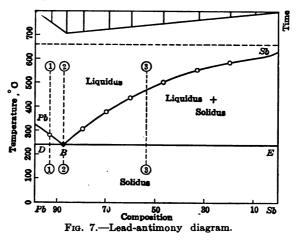


Fig. 6.—Lead-antimony cooling curves.

of the latter is lowered to a considerable extent and increasing quantities of lead still further lower the freezing point. If, on the other hand, a small amount of antimony is added to pure lead the melting point of the lead is also lowered and, as in the case of the antimony, is progressively lowered by the addition of greater quantities of antimony. The effect of the addition of each metal to the other is shown in the series of curves of Fig. 6. It is obvious that since each metal lowers the freezing point of the other, the lines connecting these freezing points must intersect at some point as shown by the dotted lines in the drawing Fig. 6. This point

of intersection is one of great interest and importance and has been called the *eutectic point*. The alloy corresponding to the composition at which the two lines intersect is the *eutectic alloy* and the temperature is the *eutectic temperature*. If the data given by the cooling curves is assembled in the form of an equilibrium diagram, as before, the diagram takes the form shown in Fig. 7. The significance of this type of diagram can be understood most readily by considering the physical changes which take place in a few special cases as, for instance,



during the cooling of alloys 1, 2, and 3 in Fig. 7. Since the V-shaped curve was obtained by connecting the freezing points of the separate alloys, it is evident that the area above the V represents a temperature range in which everything is in the molten condition. This is frequently called the *liquidus*. As the temperature of alloy 1 falls no change takes place until the line *PbB* is reached, at which temperature pure lead begins to separate. The result of the separation is to leave a solution richer in antimony than the original solution and, therefore, one which has a lower freezing point. Pure lead continues

to separate with the consequent formation of solutions increasingly rich in antimony and therefore with lower melting points. The fact that the solution from which the lead is crystallizing is of constantly changing composition is the reason for the shape of the cooling curves (see Fig. 6) in alloys of this type. The curve is not a horizontal line as in the case of a pure metal but, as it represents an infinite number of freezing points, it appears in the form of a change in the direction of the normal curve, or as a "hold" as it is often called. As the liquid from which the lead is separating becomes richer in antimony it approaches the eutectic composition indicated by B. Since this represents the lowest possible temperature at which lead and antimony alloys can solidify, it is evident that when the residual liquid finally reaches the eutectic composition the metal will solidify at this constant temperature. The same reasoning applies to alloy 3 except that in this case the antimony crystals separate first. The primary separation of antimony is followed by an enrichment of the remaining liquid with lead until the eutectic composition is reached again. At the composition 2 no change takes place until the eutectic temperature is reached when lead and antimony solidify together in the form of the eutectic mix-The line DBE (the eutectic line) represents that temperature below which the alloy is solid and is therefore called the solidus line.

To summarize the statements made above, it may be said that any alloy having a composition between D and B shows two heat evolutions on cooling, one which corresponds to the primary separation of lead and a second which is due to the solidification of the eutectic mixture. The amount of residual material having the eutectic composition is greater the nearer the composition approaches that of the point B and is zero at

point D. Along SbB antimony is the primary separation and the eutectic mixture of antimony and lead is the secondary.

Because of the constant temperature at which the eutectic separates it was formerly believed that the eutectic was a compound. The microscope shows that this is not the case but that, on the contrary, the eutectic alloy is an extremely intimate mixture of the two com-Since the eutectic is a mixture of the ponent metals. two metals and since, as shown in the diagram, the eutectic line extends from one side of the diagram to the other, it follows that while lead and antimony are wholly miscible and soluble in each other in the liquid state they are wholly non-miscible, or insoluble in each other, in the solid state. That the metals are insoluble in each other in the solid state must be true as the diagram shows that, however small an amount of either metal is added to the other, there is always the secondary heat effect at the eutectic temperature.

The practical application of the time curves is much more evident from this diagram than from the preceding As the time taken for the eutectic to solidify is greatest where there is most eutectic, it follows that the time curve has its maximum at the eutectic composition and drops to zero at the pure metals. This fact is most useful in the construction of the diagram of two unknown metals. Formerly the location of the eutectic point was a matter of repeated trials with no advance information as to the probable location of the point. With the introduction of the time-line idea the question is much simplified. It is only necessary to determine the time-lines for a few alloys. After plotting these lines on a horizontal base the ends are connected. The intersection of the two oblique lines resulting gives a close approximation to the eutectic composition so that its

exact determination, if that is desired, is a matter of a very few additional experiments.

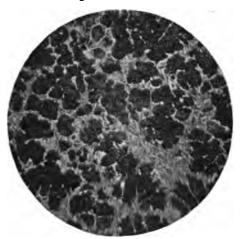


Fig. 8.—Lead-antimony alloy with excess lead. Corresponds to ①, Fig. 7 (75 ×) (HOMERBERG).



Fig. 9.—Lead-antimony eutectic. Corresponds to 2. Fig. 7 (75 \times) (Homerberg).

The microscopic structure of these alloys is exactly what would be predicted from the diagram. All alloys

from pure lead to the eutectic composition show primary lead crystals surrounded by more or less of the



Fig. 10.—Lead-antimony alloy with excess antimony. Corresponds to ③, Fig. 7 (Homerberg).



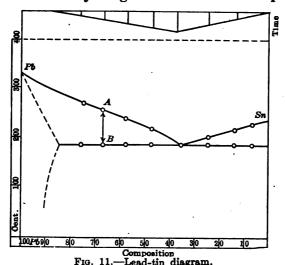
Fig. 10b.—Bismuth-tin. Eutectic with slight excess tin (SAWYER).

eutectic B, depending on the composition (Fig. 8). Alloys from the antimony side to the eutectic, show

primary antimony crystals imbedded in the eutectic (Fig. 10). The alloy having the composition B shows simply the fine-grained eutectic structure without primary crystals of either metal (Fig. 9). A better defined eutectic is shown in Fig. 10b, the Bi-Sn eutectic.

The lead-antimony alloys are commercially of much importance. Antimony is too brittle to be of use alone but because of its hardness it gives to lead properties which are very desirable for certain purposes. The alloys are used for acid proof coatings, for type and for light bearings.

The eutectic alloys of greatest commercial importance



are in the tin-lead series of which solders are made. The incomplete diagram, Fig. 11, shows those changes which are of technical interest but omits certain facts which will be considered later. Of the many mixtures used, two characteristic types are tin solder, containing about 37 per cent. lead (corresponding to the eutectic composition) and plumber's solder with approximately 67 per cent. lead. The diagram shows that between the points A and B, corresponding to a temperature drop of about 70°, the alloy consists of lead crystals supported in a molten metal. This produces the pasty consistency which makes the plumbers "wiped joint" possible.

The two examples just given illustrate in a general way the factors which are commonly determined in the study of alloys. Many other types of alloy diagrams have been worked out which deal with the formation of intermetallic compounds, solutions of one metal in another, transitions of one compound into another, either during the solidification of the alloy or after it has completely solidified, and other possible changes which may take place. Before considering these more complex alloy diagrams and their applications in practical work it will, perhaps, be simpler to study some of the methods and forms of apparatus that are actually used in the laboratory preparation and microscopic study of the alloys.

CHAPTER II

LABORATORY METHODS OF METALLOGRAPHY

The preceding chapter indicates that in the laboratory study of the alloys and in the construction of their diagrams, one of the most important factors to consider is the succession of heat changes which take place when the molten mixture of metals passes into the completely solid state. In a few cases, notably in the cooling of steel, changes of vital importance occur far below the point of solidification of the alloy so that it is necessary in special instances to follow the cooling to very low temperatures. A study of these thermal changes necessarily involves three factors: (1) A method of melting the mixed metals, (2) a container in which the metals can be melted, and (3) an apparatus for measuring temperatures and, especially, temperature changes.

1. Furnaces.—The furnaces used in the melting of metals vary so much with the amount of material to be melted and with the melting points of the metals involved that but one furnace will be described in detail. There is no difficulty, however, in building or buying small furnaces for any sort of alloy work.

For the study of the heat changes which take place in alloys of low melting point (900°C. or lower) a convenient form of apparatus is shown in the photograph Fig. 12 and given in detail in the sketch Fig. 13. A is an iron tube about 5 inches long and from $2\frac{1}{2}$ to 4 inches in diameter. It can be made quite readily by threading one end of a short piece of steel pipe and screwing on a cap. The open end is fastened to a triangle of heavy

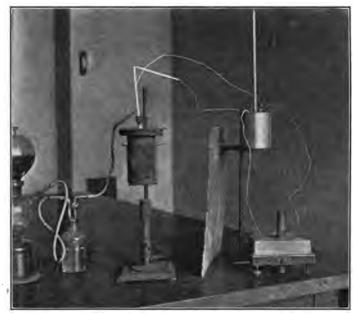


Fig. 12.—Photograph of a simple type of cooling curve apparatus.

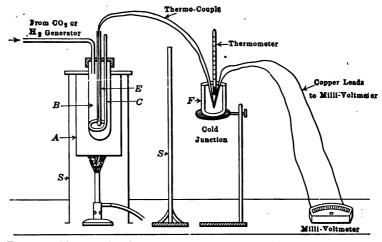


Fig. 13.—Diagram sketch of melting system and cooling curve apparatus.

iron or chromel wire so that the tube may be suspended over a burner by means of a ring and stand. The source of heat may consist of one or more Tirrell or Méker burners or, for very high temperatures, a blast lamp. The flame is protected from draught by means of a concentric cylinder of asbestos cloth separated from the outer wall of the iron tube by a space of 3/4 to 1 inch through which the gas flame can pass. This asbestos collar also retains the heat and makes the melting process easier and quicker. This simple method of heating may be replaced by any of the more elaborate types of furnaces. The more expensive wire wound electric resistance furnaces of the vertical type (dental furnace type) are much easier to control if provided with a variable resistance. For the high melting elements like nickel, cobalt, chromium and the metals of the platinum group a carbon resistance furnace is necessary, the details of construction of which may be found in any book on applied electricity. A recently developed electric furnace of the induction type promises to be of great value in the study of the high melting alloys.

2. Container for the Melted Metals.—The material and shape of the container depend on the temperature at which the alloys melt, the properties of the melted metal and the shape of the furnace. For use with the furnace just described a tube of the shape shown in B, Fig. 13, is most convenient. This tube is embedded in sand in the iron case A so that heat may be distributed to it as uniformly as possible. For alloys with a low melting point (less than 700°C.) hard glass tubes are most useful as the filling of the tube and adjusting of the temperature measuring instrument can be watched. For alloys which melt above the softening point of glass, tubes of porcelain or fused quartz are required. Thinwalled tubes of unglazed porcelain may be used for

almost all metals. In a few instances where the metal forms an oxide which is highly reactive chemically (e.g., chromium oxide or manganese oxide), it may be necessary to use the much more fragile magnesia tubes. This expedient, fortunately, is seldom needed. Tubes of this size limit the amount of alloy to be studied to about 40 grams. When larger weights of metal are to be used larger furnaces and crucibles must be substituted.

Filling the Tube or Crucible.—The metallic elements of which the alloy is to be composed are weighed in the desired proportions in the form of small chips, clippings or drillings and, in most cases in laboratory practice, are mixed before they are introduced into the tube. exceptional cases it may be necessary to melt the less volatile component first, adding the more volatile element in successive small portions. The amount of material to be used is determined by the accuracy desired in the final results. As a laboratory experiment or as a preliminary survey of the field to determine the general shape of the equilibrium diagram, 20 to 30 grams of the mixture is enough. It must be clearly emphasized, however, that where great accuracy is required and slight heat changes are to be looked for, the amount of material must be very greatly increased, often up to 400 to 500 grams. As the metals used should be of great purity and are therefore expensive it is seldom desirable to experiment with such large amounts of material.

Stirring.—There is often a marked tendency for the molten metals to separate into layers, especially if they differ considerably in specific gravities and mix with difficulty or not at all. In such cases the liquid mixture must be stirred during the course of the experiment. This can usually be done by means of a glass or porcelain rod having a circular bend at the bottom through

which the thermometer or other temperature measuring device can pass (see C, Fig. 13). This rod is moved slowly up and down during the cooling of the melted alloy.

Oxidation in the Tube.—It is necessary in all cases to protect the metals during the melting and during the solidification from the oxidizing effect of the air. In a few instances this may be done by covering the surface with powdered charcoal but it is usually more convenient and more effective to melt the metals in an inert gas. Hydrogen, carbon dioxide and nitrogen have all been used for this purpose. The gas passes from the generator into the melting tube through the bent glass or porcelain tube, Fig. 13. As a safety measure, if hydrogen is used, it is best to pass the gas through a small drying tube containing a number of disks of wire gauze. The gauze will cool the gas so that there is no danger of setting fire to the hydrogen in the generator or storage tank.

The oxidation effects are slight with the low melting metals protected in this way so that it may be assumed that the composition of the resulting alloy is the same as the composition of the mixture from which it was made. This is not the case with high melting, easily oxidized metals, even under the most favorable conditions, so that the final composition of the alloy should be determined by chemical analysis.

Weight and Atomic Per Cent.—In all industrial alloy work, and for most laboratory purposes, the metals are mixed according to their percentages by weight of the total amount of material used. It will be shown later that some metals form intermetallic compounds. In this case a system based on the atomic relationships is more convenient. For example, a compound of tin and magnesium containing 70.95 per cent. tin by weight

is known. This percentage composition gives no indication of the relation of the atoms in the compound. If now the composition is indicated in atomic per cent., it will be found to be 33.33 atomic per cent. tin and 66.66 atomic per cent. magnesium, showing at once that the formula is SnMg₂. The following expression shows the method of converting weight per cent. into atomic per cent.:

A =atomic weight of first metal;

B =atomic weight of second metal;

p = weight per cent. of A;

q = weight per cent. of B.

Then:

Atomic per cent. of
$$A = \frac{100 p}{p + q \frac{A}{R}}$$

and:

Atomic per cent. of
$$B = \frac{100 \, q \, \frac{A}{B}}{p + q \, \frac{A}{R}}$$

3. Measurement of Temperature Changes.¹—A mercury thermometer will serve for the measurement of the temperature changes with the very low melting alloys as those of sodium, potassium or the amalgams. Almost all alloy work, however, requires higher temperatures than can be determined in this way and some form of pyrometer must be used. As in the case of the furnaces, many excellent pyrometers of different sorts are obtainable. One of these pyrometers will be described as it illustrates the general method of use which may be applied with slight variations to any of the other instruments. Protected from direct contact with the molten

¹ For a detailed description of temperature measurements see "The Measurement of High Temperatures" by Burgess and Le Chatlier.

metal by a glass, quartz or porcelain tube E (Fig. 13). are two wires of different metals joined at the bottom to form the thermal junction or thermoelement. For the measurement of low temperatures one of these wires may be copper, the other constantan (a copper-nickel alloy). For somewhat higher temperatures, a thermal couple made of chromel-iron may be used. peratures up to about 1650°C., a rare metal couple. one wire of which is platinum, the other an alloy either of platinum and rhodium or platinum and iridium, is required. The two wires forming the thermal couple must be insulated from each other inside the protecting tube. This may be done by wrapping one wire with asbestos thread or by incasing it in short lengths of capillary tubing of quartz or porcelain. The loose ends of the wire pass into a jar F where they are kept either at constant temperature or at some temperature which may be determined from time to time and will not vary more than two or three degrees during the experiment. A convenient arrangement is to have these wires pass through a cork stopper into a Thermos or other vacuum walled bottle. If ice is kept in the container during the run, no correction for the temperature of the "cold junction" is needed. Otherwise, a correction for the temperature of the cold junction must be made. ends of the thermocouple are connected inside the jar F to insulated copper wires leading to the instrument G. The instrument on which the temperatures are read is commonly a millivoltmeter. Most of the millivoltmeters recommended for temperature work of this character are provided with two scales, one of which reads millivolts and the other temperatures directly, either in Centigrade or Fahrenheit degrees. The temperature scale may be used with only a single pair of metals and even then the reading varies somewhat with continued use of the couple.

so that, except for commercial work, the millivolt scale is almost always used in spite of the obvious advantages of a direct temperature reading.

In order, then, to establish the connection between the millivoltage as read and the temperature to which it corresponds, calibration is necessary. This can be most simply done by determining the melting points of a series of pure substances and constructing a plot, using the known temperatures as ordinates and the instrument readings as abscissæ. The following list of pure substances and melting or boiling points is given for convenience but any materials having definite melting points at suitable intervals may be used.

Water b. p	100
Tin m. p	231.9
Sulphur b. p	444.5
Antimony m. p	
Silver m. p	960.2
Copper m. p	1082.8

In locating the freezing points of the substances used in the calibration, it is convenient to follow the same procedure that is followed later in studying the alloys themselves. The pure substance, tin for example, is heated until it is completely melted. The supply of heat is then cut off and the melted mass allowed to cool slowly. Temperature readings are now taken at definite time intervals. If the temperature is high and is falling rapidly, intervals of five seconds are allowed between each consecutive reading of the millivoltmeter When the cooling rate is normal (about 5 to 10 degrees per minute) an interval of ten seconds between readings will show any material changes in the cooling rate. At low temperatures where the difference in temperature between the alloy and its surroundings is small, the cooling will be so slow that a much less frequent reading of the instrument is required. The frequency of

readings is a question of judgment but ten seconds between readings may be taken as a reasonable interval. If the millivoltages are now plotted as ordinates and the time intervals as abscissæ, a curve will be obtained showing a horizontal break at that millivoltage corresponding to the freezing point of the material in question. This horizontal line which indicates, not only the temperature of solidification but the time taken for the material in question to solidify, varies in length with the amount of material used and with its latent heat of fusion. The constancy of this time interval under the same conditions make its determination of great value in making the alloy diagrams.

Various types of millivoltmeters are in use, some direct reading, some of the mirror type in which the deflection is magnified by reflecting a beam of light on a scale at some distance from the instrument and still others of the recording type. Whichever instrument is used, the general method of study consists in establishing a connection between the temperature changes and the intervals of time during which these changes occur. Instead of using a millivoltmeter as a temperature measuring instrument, a potentiometer may be used. instrument requires somewhat more care and experience in operation than the millivoltmeter but the results are far more accurate. Where exact temperatures, rather than relative temperatures or rapid temperature changes are required, the potentiometer should always be used. The modern forms of potentiometer can be operated so much more rapidly than the early types that their use by metallographists is constantly increasing.

Having considered the various factors involved in the study of the temperature changes taking place when an alloy is cooled it may be helpful to summarize these factors in a brief description of an actual melting opera-

tion. Referring once more to Fig. 13 (p. 19), the process is as follows. Metals X and Y are weighed in a finely divided condition, such weights of the metals being taken as will produce an alloy of the required composition and in such amounts that with the apparatus described the total weight will be between 20 and 30 grams. These are mixed in the tube B, imbedded in sand in the furnace tube A. The stirring rod C, the gas intake tube and the thermoelement protector E pass through a cork stopper or a suitably perforated brass cap. The insulated wires pass to a constant temperature bottle F and then, by copper leads, to a millivolt-meter or potentiometer G. Heat is applied to the sand bath and the metals melted, allowing the introduction of the thermocouple tube and the stirring rod. The heat is then shut off and the temperature instrument is read at definite time intervals until all the heat changes have taken place and the hard alloy is cooling at a uniform rate. The readings are carefully recorded. study of a binary (two component) alloy this operation is repeated with a series of metal mixtures of varying composition. If the nature of the equilibrium curve is wholly unknown, mixtures are generally taken which vary in composition by 10 per cent. intervals from one pure metal to the other. These eleven points (this includes the melting points of the constituent metals) will usually indicate the general shape of the diagram, after which the necessary number of additional mixtures can be selected for study in the vicinity of the more essential points such as eutectics, intermetallic compounds or other characteristic features suggested by the preliminary survey. In simple cases a very few additional mixtures will give all the information necessary, while in the more complex alloys 40 or 50 points are sometimes needed to establish the diagram.

Plotting the Cooling Curves.—Various methods of plotting the experimental results are in use. 1 Of these methods the simple time-temperature curve is used more frequently than any other although the "inverse rate" curve has decided advantages when the heat effects

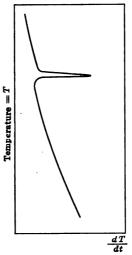


Fig. 14.—Inverse rate cooling curve. (T = temperature, t = time.)

are small. With this latter method the ordinate represents temperature as in the simple curve but the abscissa is the reciprocal of the rate of cooling, that is, the time necessary for the temperature to fall through a definite small interval (5° to 10° for example). The resulting curve has the form shown in Fig. 14 in which t =time in seconds and T =temperature in degrees.

Constructing the Diagram.—After plotting the individual cooling curves, a sheet of coördinate paper of suitable size is selected and, using percentage compositions as abscissæ and temperature holds on the cooling curves as ordinates, a diagram is constructed as indicated in Chapter I. The relative length of any hori
1 See Gulliver, "Metallic Alloys," Ed. 2, p. 175.

zontal lines that may be found in the set of cooling curves is next determined and these "time-lines" are also plotted as an independent but closely associated part of the diagram.

Preparation and Microscopical Examination of the Polished Alloys.—For the examination of the ordinary alloy, a specimen having a surface about ½ square inch is large enough. In special cases of defective material, as for instance, broken rails or similar articles, much larger pieces are needed. The small specimen for polishing is first obtained as a cubical or cylindrical piece by cutting it from the larger piece with a hack saw, or a power saw if available. Where the material is too hard to cut, as in the case of Duriron and similar high silicon alloys, the specimen is broken with a hammer and a fragment of suitable size selected for polishing. If only a very small piece of metal is available, it can be handled by placing it in a molten, readily fusible alloy and allowing the whole mass to solidify. The tiny fragment can then be polished with the larger mass of metal in which it is imbedded.

The next step in the preparation of the specimen consists in filing the surface to be examined or grinding on a carborundum wheel. If the surface is originally very rough, two or more wheels may be used to advantage, each finer than the one preceding. The subsequent operation of polishing consists in rubbing the specimen on abrasive materials of increasing fineness until a scratch-free, mirror-like surface is obtained. In polishing the specimen it should be turned through ninety degrees each time the change is made from one polishing surface to the next. The rubbing on each abrasive surface should be continued until the scratches produced by the next coarser surface (perpendicular to the direction of polishing) have been removed. The number of polishing

surfaces needed in the preparation of a specimen depends on the hardness of the material. With hard steel specimens a number of grades of abrasive material are needed each but little finer than the one preceding it, while with soft alloys like those of lead or tin very few intermediate grades of polishing material are required.

For the average specimen the following sequence of abrasives will serve: coarse file, fine file, very fine emery wheel, emery papers (French emery "Marke Hubert" is best) 1C, 1F, 0, 00, 000 and 0000. In using the finer grades of emery paper, from 00 down, a drop of oil should be applied to the surface of the specimen. From this point the abrasion is carried out by finely divided powders used in the form of aqueous suspensions which are sprinkled from time to time on the finest quality of broadcloth or chamois skin. An excellent series of polishing powders has been prepared especially for metallographic purposes by the Norton Alundum Company of Worcester. Three powders that will answer for most purposes are 60 minute emery or carborundum, followed by "alundum F" and finally by "levigated alumina." Many metallographists prefer jeweler's rouge as a final polishing agent rather than alumina. Rouge gives a brilliant final polish but has the disadvantages: (1) that it tends to cause a slight flowing of the surface metal. especially with the softer alloys; and (2) that it is a dirty and unpleasant abrasive with which to work.

Polishing may be done by hand if necessary but the operation is a long and tiring one so that machine polishing is to be recommended if an apparatus is available. For hand polishing, the various grades of paper and the cloths which are to be used as bases for the polishing liquids are tacked to smooth boards (3 inches \times 8 inches is a convenient size).

Many excellent polishing machines are now obtain-

able. They differ somewhat in detail but all consist in general of rotating disks of wood or metal over which the abrasive paper or cloth is stretched. Machines having disks revolving in a horizontal plane are more convenient to use than those of the vertical type. The liquid suspension of abrasive powder may be applied to the cloth by means of a camels hair brush, by a wash bottle or by the simple shaking bottle suggested in the sketch, Fig. 15.



Fig. 15.—Flask for suspended abrasives.

Scrupulous care in the use of polishing papers and powders must be taken to avoid the transfer of a coarse abrasive to a finer surface. A single particle of grit on the final polishing wheel may injure an otherwise perfect specimen so that repolishing is necessary.

Etching is a selective chemical action which will feet one constituent of the alloy more than the other and its purpose is to develop the internal structure of the polished alloy. The number of etching solutions which have been used is very large and varies from simple reagents like dilute acids to extremely complex mixtures for special purposes. The special etching agents used in the examination of brass and bronze and of steels will be considered later in connection with the study of these important technical alloys. For general

¹ A detailed description of mechanical polishing devices will be found in SAUVEUR, "Metallography and Heat Treatment of Iron and Steel," Ed. 2, p. 54 et seq.

purposes dilute acids (2 per cent. nitric or hydrochloric) or dilute alkalis (sodium hydroxide or ammonium hydroxide) are used. One of the most successful general reagents is made by dissolving 10 grams of ferric chloride (FeCl₃) in 100 cc. of alcohol. It will be realized that etching is a chemical problem so that the particular reagent used, as well as its strength, depends on the chemical solubility of the components of the alloy. For this reason specific directions cannot be given. most cases, however, the problem is one which is readily solved by a few trials if the effect of the reagent is watched under the microscope. Etching is most uniform if the specimen is immersed face upward in a shallow dish containing the reagent. The formation of gas bubbles on the surface must be prevented by keeping the dish in constant rocking motion or by swabbing the exposed surface with a bit of absorbent cotton at frequent intervals. After etching, the surface is washed with water and with alcohol and is dried either with cotton or by a warm blast of air. Perfectly dried specimens may be kept in a desiccator for a long period without change. Specimens may be preserved indefinitely by coating them with cellulose acetate.

For etching spots on a large surface or as a rapid method for determining the most suitable etching agent for a given alloy, a small swab of cotton moistened with the reagent may be used.

The Microscope. The polished and etched surface of the specimen must be examined by reflected light. If a low power objective is used (magnifying less than 25 diameters), a beam of light can be reflected on the surface in an oblique direction, passing below the objective. As the magnification increases the distance between the objective and the surface becomes so small that

¹ See Sauveur, "Metallography and Heat Treatment of Iron and Steel, Ed. 2, p. 67.

this method of illumination is impossible. In such cases the microscope must be provided with a "vertical illuminator," the principle of which is shown in Fig. 16. The beam of light, coming from a small arc lamp, a nitrogen filled tungsten or other powerful light source, passes into the side arm of the illuminator and is reflected by a prism or plate down to the surface of the speci-

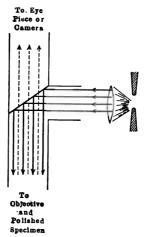
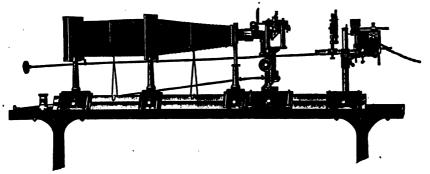


Fig. 16.—Sketch of vertical illuminator (sheet glass type) dotted lines show the direction of rays reflected from the specimen.

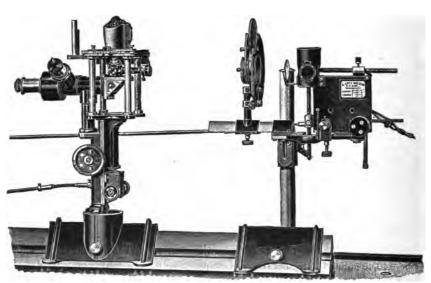
men, illuminating a spot on the surface so intensely that it can not only be examined but photographed. Such an illuminator can be fitted to any microscope but, where much metallographic work is to be done, one of the regular metal microscopes will be found much more convenient and effective. The magnifications most commonly used are 5x, 10x, 50x, 75x, 100x and 200x. In rare cases, with extremely fine-grained structure, a magnification of 500x or even 1000x may be necessary. As a matter of permanent record and for purposes of comparison of samples from different sources, photographs of the etched surfaces are often made and all

modern metal microscopes are provided with a photographic attachment.

Photographing Metal Specimens.—The beam of light



A.—The complete metallographic camera.



B.—Enlarged section showing the illuminator and microscope.
Fig. 17.—The Leitz metal microscope.

from the polished specimens can be reflected to the eyepiece for visual examination or it may pass through the bellows of a camera to a sensitive plate. The preceding cuts, Fig. 17 a and b, show the arrangement of the Leitz metallographic microscope. It is very similar to other metal microscopes and illustrates the general principles of them all.

Plates.—For making microphotographs the chief requisites of good plates are color sensitiveness and fine grain. With steel samples in which the surface of the specimen is light, with black or gray markings, the inexpensive "Stanley" plates will be found satisfactory. For colored specimens, like brasses and bronzes for example, a more color-sensitive plate has to be used. The "Wratten M" plate gives excellent results. It has the disadvantage that it cannot be handled near the ordinary dark room light but must be manipulated either in absolute darkness or by a special "safe light." "Standard Orthonon" plates, also made by the Eastman Company, are effective both for steel and for brass photo-The author has found the "Wellington Ortho Process" plates very satisfactory for all purposes and they can be handled without danger near a fairly bright ruby light. In photographing colored metal surfaces a color screen of some sort and a piece of ground glass are generally placed between the illuminating lamp and the specimen to be photographed. The color screen increases the contrast between the components while the ground glass is to diffuse the light and prevent the reflection of the hot carbons of the arc on the photographic plate. A vellow-green screen gives excellent results in photographing the yellow alloys of copper.

Exposure of the Photographic Plate.—The time of exposure may vary from a few seconds to ten or fifteen minutes depending on the source of light, the nature of the specimen, the color of the screen and the kind of plate used. The operator soon recognizes these factors so

that he can estimate the length of exposure with considerable accuracy. When the conditions are entirely unknown the following test method will save time and plates. Expose as usual for a few seconds. Instead of shutting off the light, as would ordinarily be done, push in the opaque screen, which is used to cover the plate in the holder, about one-half inch (1/2 in.) in order to shut off a portion of the exposed plate. After another short interval push in the screen another half inch. Repeat this operation until the opaque screen has been pushed into place in the holder. When the plate is developed it will show a series of bands each of which represents an exposure for a somewhat longer time than the one preceding it. Select the correctly exposed strip from the banded negative, record its time of exposure and use substantially the same length of exposure for photographs taken under similar conditions.

Development of the Exposed Plates.—Directions for the preparation of developing solutions will be found in each box of plates. Tray development requires much experience for complete success so that the use of a developing tank is strongly recommended. The operation of the tank is simple and the results are positive and uniform. Of the many kinds of developer on the market it is probable that pyro-soda will give the best results for metallographic work. After the development is completed, the plates are placed in saturated "hypo" (sodium thiosulphate) solution until the white opaque coating has dissolved and the negatives have become transparent. The clear negatives are then washed in running water for an hour, after which they are placed in a drying rack and allowed to become perfectly dry and hard.

Printing, Finishing and Mounting.—Photomicrographs require the greatest possible detail in printing so that a glossy printing paper is commonly used. Glossy Velox,

Glossy Cyko or other papers of the same sort give excel-Printing directions are always inclosed lent results. with the paper. After the prints are washed a brilliant finish is obtained by placing them face down on a ferrotype plate. To keep them from sticking to the surface of the ferrotype plate it must be cleaned before use with a solution of beeswax in benzol or by a prepared cleaner such as the Ingento Polishing Compound. After the prints are in position on the plate the surplus water is removed by means of a print roller (squeegee) and they are then allowed to dry. The dry prints are then mounted on suitable cards for examination and filing. Dry mounting tissue is excellent for this purpose. Plates, paper, mounting tissue, etc., can be purchased of any dealer in photographic supplies. If many photographs are to be taken printed cards of the general style shown in Fig. 18 will be found almost indispensable.

In addition to the thermic and microscopic methods of alloy study, other properties of alloys are occasionally used in determining their constitution. Among these less important properties are electrical and heat conductivity, heat expansion, and magnetic effects. An excellent discussion of the connection between these different properties and the equilibrium diagram will be found in Desch, "Metallography," Ed. 2, p. 230.

In closing this chapter on the methods of alloy study it must be stated that the mechanical testing of the metals for tensile strength, hardness, elongation and other physical properties is of great and constantly increasing importance to the practical metallographist. A discussion of this phase of the subject is beyond the scope of this book and the reader is referred to Rosenhain, "Physical Metallurgy," in which the methods of mechanical testing are considered in detail.

NUMBER 691

C ź LBS./80.IN. LBS./89.IN. showing crystal distortion and a crack due to WHAOH and Hads Cold worked brass & CONTRACTION overstrain. TENSILE STRENGTH ETCHED WITH ELONGATION YIELD POINT HARDNESS Cartridge brass. 2 MATERIAL

Fig. 18.—Micro-photograph mounting card. 5" X 7" is a convenient sise. 500 4-18 MICRO-PHOTOGRAPH MOUNT

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CHAPTER III

THE ALLOY DIAGRAM AND ITS MEANING

In Chapter I the construction of two simple alloy diagrams was outlined. The first was the diagram representing the melting of two metals which do not dissolve in each other either in the liquid or solid state. The second, usually referred to as the eutectic diagram, represented graphically the behavior of two metals which do dissolve completely in each other in the liquid (molten) state but are wholly insoluble in the solid state.¹

The Solid Solution.—A third relationship which may exist between metals is a partial or complete solubility of one metal in the other in the solid state as well as when the metals are molten. This relation is known as the formation of "solid solution" or, less correctly, "mixed crystals." The solid solution differs from the liquid solution simply in its physical condition. Like a liquid solution it is perfectly homogeneous and may be unsaturated or saturated. Metal A may retain 10 per cent. of metal B in the solid state but if an attempt is made to add 12 per cent. of B to molten A the solid which separates on cooling is a saturated solid solution of 10 per cent. B in A. The excess B remains in the liquid to separate later as part of a eutectic mixture, as a constituent of an intermetallic compound, or in some other form. This conception of the solid solution of two metals as wholly analogous to the liquid solution makes the graphical representation simple.

¹ It is probably not true that any two metals are wholly insoluble in each other in the solid state but in many cases the solubility is so small that it escapes detection.

Consider as an example the diagram of the alloys of copper and silver (Fig. 19). This differs from the simple eutectic diagram shown in Fig. 7 (p. 11) only in the location on it of the lines $Ag-\alpha$ and $Cu-\beta$, the significance of which is merely that molten silver, in which copper has been dissolved, is able to retain about 6 per cent. of it after the silver has solidified and that molten copper, in its turn, is capable of retaining an equal amount of silver in the solid state. When an alloy of silver and

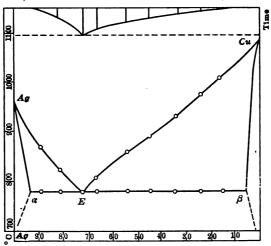


Fig. 19.—Copper-silver diagram (Heycock and Neville, Fredrich and Leroux).

copper containing less than 29 per cent. copper is allowed to solidify, the crystal which first separates is not the pure element, as in the case of the separation of lead on cooling lead-antimony alloys, for example, but is a homogeneous, crystalline solution of copper in silver. The behavior of solid solutions during the actual solidification process will be considered shortly. The significance of the diagram, then, is as follows. Any alloy of silver and copper containing less than 6 per cent. of copper, on the one hand, or less than 6 per cent. of

silver on the other, will solidify as an unsaturated solid solution which is perfectly homogeneous and under the microscope shows only the fine polyhedral lines characteristic of a single crystalline solid (Fig. 8, p. 14). now the amount of copper added to the silver is ever so slightly in excess of 6 per cent., the solid alloy is no longer homogeneous but shows a second structure element, in this case the eutectic E. It is evident, then, that in the range between the points α and β , the diagram is exactly analogous to the simple eutectic of lead and antimony, the only difference being that with silver and copper alloys the constituents of the eutectic are not the pure metals as with lead and antimony but are the saturated solid solutions α and β . The extent of solubility of the metals in each other may be determined in two ways. First, since there is no separation of a second crystal form until the concentrations represented by points a and β are exceeded, it follows that no evolution of heat will be noticed on the cooling curve at the eutectic temperature (778°C.) until the limit of solubility has been passed. Or, conversely, if a horizontal line is drawn through the points locating the eutectic temperature. the ends of the line will be found at points α and β , the The second method of limits of the solid solution. locating the limit of solubility in the solid state is microscopic examination. The microscopic appearance of the copper-silver alloys is exactly what would be expected from the diagram. From 100 per cent. silver to 94 per cent. silver the solids are homogeneous. From 94 per cent. silver to 71.9 per cent. the solid alloys show gradually decreasing quantities of the solid solution a imbedded in the eutectic E. From 71.9 per cent. to 6 per cent. silver the solid alloy shows gradually increasing amounts of the solid solution β imbedded in the same eutectic E and from 6 per cent. silver to pure copper

the alloys are once more homogeneous. When the limit of solubility is reached, the addition of the slightest excess of either metal to the other forms an alloy which is no longer homogeneous under the microscope.

The silver-copper alloy is one of great commercial importance as it is the alloy of which silver coins are made. American coins and those of several European countries contain 90 per cent. silver and 10 per cent. copper. British coinage is, however, slightly richer in silver, containing 92.5 per cent. Several alloys of the same type are known, among them aluminum-tin, bismuth-tin, cadmium-tin, but except for the silver-copper and aluminum-tin, none are of technical importance. Aluminum with a low percentage of tin has been used to a limited extent in making light castings but is unsatisfactory because of its ready corrosion.

The solubility of one metal in another may increase. as shown in the series of diagrams in Fig. 20, until the condition indicated in D is realized. The line $\alpha-\beta$, representing the secondary or eutectic separation, has gradually shortened with the increase in the mutual solubility of the two metals until in the alloy D the line has disappeared wholly, showing that the metals are soluble each in the other in all proportions. Diagrams A and D differ radically in this respect that, although both show the two metals to be soluble in each other in all proportions in the liquid state and, also, that each metal lowers the melting point of the other, diagram A indicates that the two metals are completely insoluble in each other in the solid state while diagram D shows that the metals are completely soluble in each other in the solid state. Alloy E in diagram A is as inhomogeneous as possible while $\alpha\beta$ in diagram D is perfectly homogene-

¹Law, "Alloys and Their Industrial Applications," Ed. 2, p. 272,

ous and represents simply that one of the series of perfect solutions which has a melting point lower than any of the other solid solutions in the series. This is often referred to as the solid solution minimum.

It is worth while to consider briefly the way in which such a solid solution is formed during the cooling of the

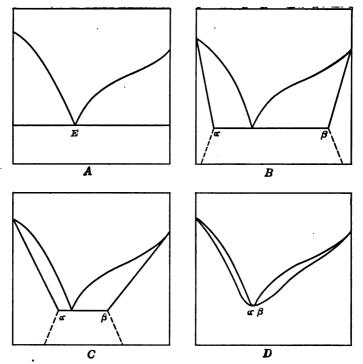


Fig. 20.—Development of the solid solution.

liquid metal. The relations between copper and manganese are shown in Fig. 21. When an alloy containing 62 per cent. manganese and 38 per cent. copper is at the temperature represented by the point z it is completely liquid. When the point b is reached the alloy begins to solidify. The fact, however, which distinguishes between the cooling of an alloy which is to form a solid

solution and a simple eutectic alloy is that the crystal which first separates, in this case at point b, is not a pure metal but is a solid, the composition of which is represented by the point b^{I} . That the crystal b^{I} which separates from the molten metal at b actually differs from the liquid in its composition may be determined by the removal of some of the crystals after the alloy has

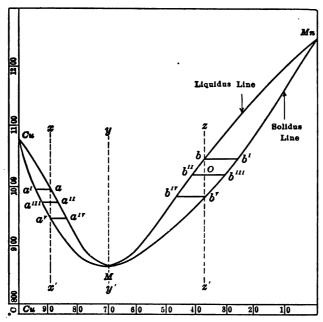


Fig. 21.—Copper manganese alloys.

partially solidified. The crystals and the remaining metal are then analyzed. In the case of Mn-Cu, the crystals will be found considerably richer in manganese than the liquid from which they are removed. As the mass cools the composition of the crystals changes along the line b_1b_V , while the liquid varies in composition along the line bb^{IV} . Referring to these conditions in terms of

equilibrium it is said that crystal b^{I} is in equilibrium with liquid b, crystal b^{III} with liquid b^{II} and crystal b^{V} with liquid b^{IV} . In other words at the temperature represented by the line $b^{I}b^{III}$ crystals of b^{III} will stay unchanged indefinitely in a liquid of the composition b^{II} . This stable relationship between crystal and melt would not exist between b^{II} and b^{III} if the temperature was changed in the slightest degree. Nor, if the temperature was kept constant could any manganese-rich liquid and solid of different compositions than those corresponding to b" and b" exist together. The fact that $b^{\rm I}$, $b^{\rm III}$ and $b^{\rm V}$ represent solids in equilibrium with liquids b., b^{II} and b^{IV} respectively has given the name solidus curve to the line connecting the points b, b, b, and liquidus curve to the line b, b^{II}, b^{IV} connecting those points which represent the composition of the liquids with which these solids are in contact.

It is necessarily true that the crystal which solidifies last (b^{V}) must have exactly the same composition as the original liquid melt (b). The perpendicular line $b-b^{V}$ connecting these two points is one of great importance in interpreting the diagram, as it makes it possible to state the relative quantities of liquid and solid that can exist together at any given temperature within the solidification range. It is obvious that the amount of crystal b^{I} existing in the presence of liquid b is infinitely small and equally obvious that the amount of liquid b^{IV} existing in contact with the crystal b^{V} is also infinitely small. Between these extremes lie an infinite number of relationships between solid and liquid. These relationships, however, are graphically represented by the horizontal distances, left and right, from the line b, b^V to any pair of liquid and solid phases in the series. As a specific illustration, it is true that the quantity of crystal b^{III} is to the quantity of liquid b^{II} inversely as the

distances from these points to the line b, b^{V} or as ob^{II} is to ob^{III} .

The nature of the solidification of a solid solution crystal naturally determines the shape of its cooling curve. When a pure metal or a eutectic mixture solidifies, the crystal separating and the liquid from which it separates have the same composition and, following well established laws, the temperature stays constant during freezing and appears as a horizontal line on the temperature-time curve. In the freezing of solid solutions, however, the solidifying crystal changes its composition constantly as does the solution from which it is crystalliz-

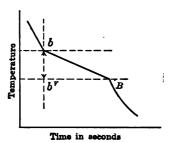


Fig. 22.—Type of solid solution curve.

ing. The solidification, then, is not that of a single solution but of an infinite number of solutions and the solutions formed have a corresponding number of melting points. The effect of this sort of freezing is to produce a curve which shows not a horizontal freezing line, but an oblique line indicating a change in the normal cooling rate during the solidification interval. The normal curve of a solid solution alloy is shown in Fig. 22 in which point b represents the beginning of the freezing and point b the end, after which the normal cooling rate is resumed. The perpendicular distance between b and b is shown by the line b and represents the temperature drop during the process of solidification. Point

b, then, represents one point on the liquidus curve, Fig. 21, and B, or b^{V} a point on the solidus curve. By constructing a number of freezing point curves and determining the temperatures at which freezing begins and at which it ends in each, the liquidus and solidus lines can be located.

In the manganese-copper diagram, Fig. 21, the relationships along the line xx' are wholly similar to those just described except that the primary separation is a copper-rich crystal. The alloy having the composition y (copper 70 per cent.—manganese 30 per cent.) is unique in that it is the only one of the series in which the composition of the crystal first separating is the same as the liquid melt from which it comes. The freezing which takes place at M is, therefore, analogous to the freezing of a pure metal and its cooling curve is represented by two sloping lines connected by a horizontal.

Microscopic Appearance.—The microscopic appearance of solid solutions is often misleading but is readily explained. If perfect equilibrium conditions are reached, the solid solution should, and does, resemble a pure Consideration of the method of freezing makes metal. it clear that, unless time is allowed for the readjustment of the varying crystal concentrations during freezing, the crystal has a duplex rather than a homogeneous structure. In the case of manganese-copper, rapid cooling of a copper-rich mixture produces an alloy showing leaflike masses of a copper-rich alloy imbedded in a groundmass of manganese alloy. A true solid solution can always be made homogeneous by annealing, i.e., heating for a long period at some temperature below the melting point of the crystal, so that opportunity is given for the concentrations of the duplex crystals to equalize each other by diffusion.

A limited use has been found for copper-manganese

alloys of high copper concentration in firebox stay bolts. An alloy containing 82 per cent. copper, 15 per cent. manganese and the rest nickel and iron is the interesting alloy, Manganin, which has a very high electrical resistance and a temperature coefficient of almost zero.

A second type of solid solution diagram which might be expected would be one in which the addition of each metal to the other *raised* both melting points producing a solid solution curve with a maximum. This type has not been found in practice.

A third and very important type of solid solution includes that class of alloys which are mutually soluble

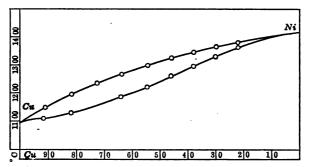


Fig. 23.—Copper-nickel alloys (Guertler and Tamman).

in all proportions but whose diagrams show neither a maximum nor a minimum. A relation of this sort is shown in the copper-nickel alloys, Fig. 23. The mechanism of cooling is exactly the same as in the case of the copper-manganese alloys, except that there is no alloy in the series which on crystallizing has the same composition as the liquid from which it comes. These copper-nickel alloys are of great technical importance. Some compositions are used for copper coins, an alloy containing 20 per cent. nickel is used for capping rifle bullets and the alloy 60 per cent. copper and 40 per cent. nickel has high electrical resistance and a low

temperature coefficient. Under the name Constantan this latter is often used for electrical purposes and coupled with copper or iron wire forms an excellent thermocouple as was stated in the previous chapter (p. 24). One of the important Canadian ores is of such a composition that, on smelting, there is produced a copper-nickel alloy containing about 67 per cent. nickel, 28 per cent. copper and a small amount of iron and manganese. The alloy is known as Monel metal and has very great tensile strength, high ductility and remarkable resistance to corrosion.

That group of alloys in which the constituents show more or less complete solubility in each other includes by far the greater number of the technically important alloys. Steel, brass and the bronzes all belong in this class and will be discussed in detail in later chapters. Brief reference must be made here to a few of the less commonly used alloys of this class which are, nevertheless, very important technically. Gold, with dissolved silver, is the basis of gold coinage and jewelry. gold used to imitate platinum is an alloy of gold with about 18 per cent. of nickel. Of interest to the chemist are Palau, the palladium-gold alloy used as a substitute for platinum, nichrome or chromel the highly resistant nickel-chromium solid solution much used in triangles for laboratory use, for crucible tongs and in heating coils for electric furnace work, and stellite the cobaltchromium alloy which because of its remarkable nonrusting properties finds varied uses in the manufacture of cutlery, surgical instruments and the like.

Intermetallic Compounds. —A large number of alloys contain or consist of definite intermetallic compounds of which more than three hundred have been found. With few exceptions, these alloys are technically unim-

¹ Desch, "Intermetallic Compounds."

portant as they are for the most part hard, brittle and almost wholly lacking in strength and ductility. They are interesting chiefly from the viewpoint of the student of valence as many of the compounds, while relatively simple, show valence relations differing greatly from those that have been generally accepted, as for example, Na Zn₁₁.

The effect of the existence of a compound on the shape of the equilibrium curve depends on whether the compound does or does not decompose into its elements before its melting point is reached. If the compound does not decompose before it melts, the diagram is of the open maximum type. If it does decompose before the melting point is reached, the diagram is said to show a concealed maximum or to be of the transition type.

The Open Maximum.—The alloys of tin and magnesium illustrate the first type. Assume for the purposes of discussion, that magnesium and tin do unite to form the compound $SnMg_2$ and that this compound, which is homogeneous and behaves in every way like a pure metal, is completely miscible both with magnesium and with tin in the molten state but wholly insoluble, in both, in the solid state. In such a case we would be dealing with two systems of the simple eutectic type as shown in Fig. 24, A and B.

If these two simple diagrams are combined as in Fig. 24, C the result is a typical compound diagram showing a maximum at a point corresponding to the compound $SnMg_2$. In laboratory practice there are four indications of the existence and composition of a compound of this type. Representing the two metals as A and B and the compound as AmBn and assuming that AmBn does not dissolve either A or B to form a solid solution, it will be seen that:

- 1. The compound AmBn lies at the maximum of the curve.
- 2. The eutectic temperature-hold corresponding to a eutectic between AmBn and A becomes zero at A and at the composition AmBn.
- 3. The eutectic between AmBn and B also disappears at AmBn.

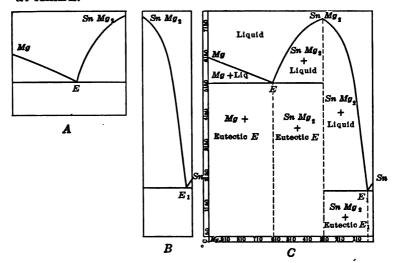


Fig. 24.—Development of open maximum type diagram (Tin-magnesium alloys—Grube).

4. The alloy corresponding to AmBn is the only one which is microscopically homogeneous.

Unfortunately the methods of locating the compound are seldom as exact as in this case. Far more often the compound will dissolve one or both of the metals from which it is made, to form solid solutions, as indicated in Fig. 25. Under these circumstances criteria 2, 3, and 4 disappear as neither eutectic E_1 nor eutectic E_2 ends at the composition AmBn and (4) the alloy is homogeneous not only at AmBn but throughout the entire range between D and F. In such a case the intersection

of the maximum curve with its tangent, drawn parallel to the concentration axis, indicates the composition of the compound. This point will invariably be found to lie at, or very near, a composition corresponding to a simple atomic relationship.

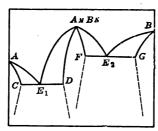
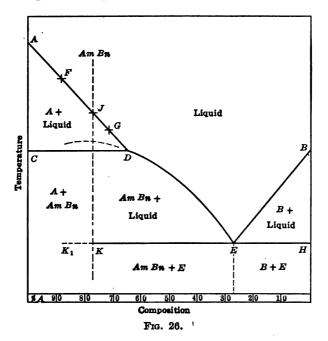


Fig. 25.—Open maximum type with solid solutions.

The Concealed Maximum.—This is perhaps the most difficult of all alloy types to understand and because of experimental difficulties, to be referred to shortly, is the hardest to construct. An ideal case is illustrated in Fig. 26.

The elements A and B unite to form a compound AmBn but, instead of melting as a homogeneous substange the compound decomposes into its elements at a temperature, CD, below its melting point. The result is that, instead of passing directly from a solid compound into a molten metal, it changes at the temperature CD, into a liquid of composition D and a solid of different composition from the original solid, namely, the metal A. Conversely, when a mixture of the composition AmBn is cooled from a liquid the following changes take place. The temperature falls normally until the point J on the line AD is reached. Here, as the diagram shows, pure A begins to separate and the concentration changes in the usual way until the point D is reached. The temperature has now fallen to that point at which the compound AmBn can exist and the tendency for it to

form is so great that a reaction takes place between the solid crystals of A which are in suspension and the liquid of the composition D. Since the crystals A are obviously far poorer in B than is the compound and since the liquid D is much richer in B than the compound, a reaction between the two to form the compound causes the complete disappearance of both. If the original



mixture has a composition, F, richer in metal A than the compound, not all of the A crystals can be used up by the liquid D and the solid alloy is a mixture of A and AmBn. If, on the other hand, the original mixture has the composition G, containing less A than corresponds to the compound, it follows that the A crystals which separate first along the line CD will be wholly dissolved by the liquid D and a certain amount of excess liquid will be

left. Crystallization then proceeds along the line DE until the eutectic (a mixture of AmBn and B) is reached.

Since D represents that point at which the pure metal A reacts with the liquid and is transformed into the compound AmBn, D is often called a transition point and AmBn a transition product.

As was the case with the open maximum, there is no difficulty in locating the compound in the ideal type of concealed maximum just considered, because the temperature change corresponding to the eutectic E is zero at the composition of the compound, and, as in the first case, the compound is the only homogeneous alloy in the series. The time during which the temperature stays constant, while the transformation on the line CD is taking place, is longest under ideal conditions at the composition of the compound, dropping to zero at points C and D.

Solid solutions complicate the concealed maximum diagram as they do the open maximum diagram but there is the additional serious difficulty of incomplete transformation at the point D. This is readily understood from the nature of the reaction taking place at this point. The pure crystals of A begin to dissolve in liquid D to form the compound. This formation takes place on the surface of the crystal and not infrequently the compound forms a coating around the crystal protecting it from further reaction with the solution D as indicated diagrammatically in the sketch, Fig. 27, and actually in the photomicrograph, Fig. 28.

This phenomenon is known as surrounding and makes the location of the compound exceedingly difficult for several reasons. First, the time during which the temperature remains constant at the transition point, which normally is longest at the composition of the compound, is greatly reduced if the transformation is incomplete and instead of decreasing regularly to the left and right of the compound, changes so irregularly that the time curve is of no value. Second, since more of the liquid is left than corresponds to true equilibrium, the eutectic line HEK, Fig. 26, extends to the left of its normal limit in some such way as in indicated by the dotted line KK_1 . Finally, the alloy, even though it corresponds to the compound, may show three structure elements, Fig. 27. In a case of this sort practically all that can be done to

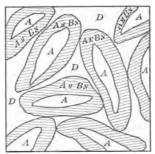


Fig. 27.—Sketch illustrating the phenomenon of surrounding.



Fig. 28.—Antimony 50 per cent. Tin 50 per cent. Shows SbSn inclosing crystals of antimony. The black ground mass is a tin-rich solid solution.

locate the compound is to anneal a series of alloys in the neighborhood of the compound and determine which one of the series becomes homogeneous. Should several alloys in the series become homogeneous, indicating the existence of solid solutions, the determination of the composition of the compound is practically impossible.

The hardness of the intermetallic compounds is their most useful property and is made use of in the few technical alloys in which they are found. In bearing metals, for example, where a small amount of hard material not easily worn down by abrasion is desired, the compound Cu₃P is found in phosphor bronze and the

compounds SbSn and Cu₃Sn in Babbitt metal. By far the most important of these compounds is the iron-carbon compound Fe₃C, the chief surface constituent of case hardened steel, the preparation of which will be considered later.

Changes in the Solid Alloy.—The diagrams which have been considered so far have dealt with changes which occur when the alloy passes from the liquid to the solid state or vice versa. Some of the most valuable technical alloys, notably steel, acquire their properties or modify them materially by changes which take place in the solid state. Iron, for example, is believed to exist in at least three allotropic forms, α -iron stable below 780°, β -iron existing between 780° and 900° and, finally, γ -iron stable above 900° and practically non-magnetic. While these magnetic changes are of interest to the physicist, the fact of importance to the metallographist is that γ -iron will hold carbon in solid solution and that α -iron will not. This means that, when the iron-carbon alloy is cooled. a change in components, and therefore in physical properties, occurs in passing from the γ -iron to the α -iron range even though the alloy in the γ -field is perfectly solid.

More important than changes due to the allotropism of a single metal are those changes which come from the decomposition of a solid solution at temperatures below its freezing point. All the changes which can take place when a liquid solution freezes may also occur when a solid solution decomposes. It may change to a eutectic-like mixture or to another solid solution more or less complete, or it may decompose to form one or more compounds. Some of these possible changes are indicated in the sketch, Fig. 29. The most important of these transformations in the solid state is that shown in A of this sketch as many of the valuable properties of steel, given

to it by heat treatment, are due to a decomposition of this sort. Although the details will be given later it may be said that the transformation from a solid alloy of the solid solution type to one of a different character requires a definite amount of time and, by shortening the time, this transformation can be partially or wholly suspended. For example, by suddenly cooling (quenching) an alloy from the temperature indicated by x in Fig. 29,I, it is possible to prevent the transformation along AE of the solid alloy into that represented by x' with the result that at ordinary temperature the alloy

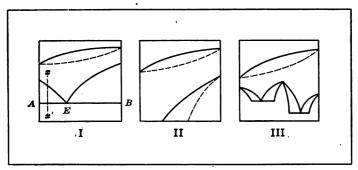
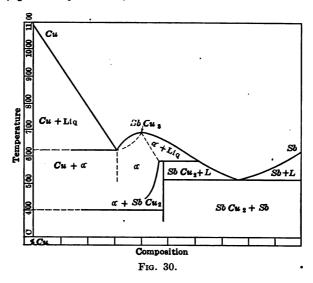


Fig. 29.—Types of changes occurring in the solid state.

exists in the condition which it had at the higher temperature x. The physical properties of a solid solution are so different from those of a eutectic-like mixture that by more or less completely checking the change from x to $x^{\rm I}$ the mechanical properties of the alloy can be profoundly modified and can be controlled within fairly definite limits. The alloy represented by the point E, Fig. 29,I, has all the characteristics of the eutectic mixture which separates from a liquid solution. Since the separation takes place from a solid solution, however, the name eutectoid is commonly given to it.

Many binary diagrams of a much more complex character might be discussed but all of them are combina-

tions of the simpler diagrams and can be constructed or interpreted without difficulty. It is only necessary to break down the complex diagrams into the simpler elements of which they are composed in order to make them perfectly clear. As a single example of a combination diagram that of the copper-antimony series of alloys may be noted, Fig. 30. In this is found the open maximum, probably SbCu₃, the concealed maximum SbCu₂,



a eutectic mixture of SbCu₂ and Sb and a series of solid solutions, α. Examination of this fairly complex diagram shows clearly what combinations are to be expected at different temperatures and at varying compositions.

Ternary Alloys.—The alloys of three or more metals form a large and, to a great extent, unworked field of metallography. The experimental work, while no more difficult than for the binary mixtures, is much more expensive and time consuming because of the large number of experiments needed to establish the relationships. The study of ternary systems will be extended

in time and will, doubtless, lead to the discovery of interesting and commercially important alloys.

Anything like a complete discussion of ternary diagrams is beyond the scope of this book but a single example will be considered to show the methods of representing these alloys and the way in which the diagrams are constructed from experimental data.

It is evident that the relation of three metals cannot be represented in a plane as in the case of the binary alloys. The easiest way to visualize these relationships is, perhaps, in the form of a space model, Fig. 31, on a triangular

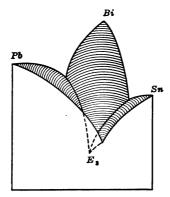


Fig. 31.—The ternary solid (the intersection of the dotted lines E_i is the ternary eutectic).

base, the corners of which represent the three component metals, while the perpendiculars to this triangular plane represent the temperatures. Such a method of representation has many disadvantages. It is difficult to construct mechanically and unsatisfactory in that it shows only the liquidus surface, *i.e.*, the surface on which solids begin to form, and gives no idea of the changes which take place beneath the surface. A more satisfactory method consists in the projection on a triangular surface of a series of contour lines indicating temperature

changes. Such a figure, together with a series of triangular diagrams showing the conditions which exist at varying stages of the crystallization will usually be enough to indicate the various products formed.¹

In the graphic representation of a triple alloy the first step is a means of showing the composition of any given

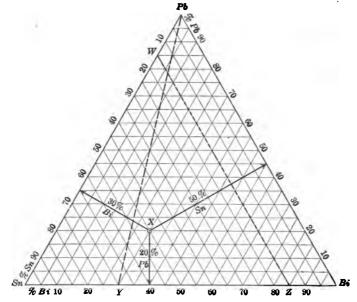


Fig. 32.—Method of showing the composition of ternary alloys.

mixture. This is done most easily by the use of plotting paper with triangular coördinates. The classic example of the simple ternary is the series composed of lead, tin and bismuth. In the diagram, Fig. 32, the three corners represent the pure metals. The base of the triangle of which each metal is the apex represents therefore zero concentration of that element. For example, the line

¹ An excellent discussion of Ternary Alloys will be found in GULLIVER, "Metallic Alloys," Ed. 2, p. 340, from which much of the following material is taken.

Pb-Sn represents zero per cent. Bi, the line Pb-Bi zero per cent. Sn and Bi-Sn is zero per cent. Pb. Starting with these lines as bases and approaching the element whose percentage is desired, each line parallel to the base indicates one per cent. assuming, as is usually the case, that the triangle is divided by 100 parallel lines in each of the three directions. Point X in the figure therefore represents 20 per cent. Pb, 50 per cent. Sn and 30 per cent. Bi.

A study of the geometry of this figure shows two other facts which are of importance in the actual construction

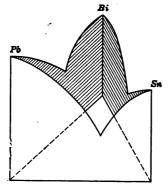


Fig. 33.—Combination of the binary surfaces—Pb-Sn, Sn-Bi and Bi-Pb.

of these diagrams. A line drawn from any corner to any point on the opposite side represents an alloy in which two of the metals have a constant relationship to each other while the percentage of the third metal varies. Pb-Y, for example, is a line on which the relation of tin to bismuth is always 7 to 3. A line parallel to one side of the triangle represents an alloy in which one metal has a constant percentage while the other two vary. On WZ the per cent. of Sn is always 15 per cent. while the lead increases from zero per cent. at Z and the bismuth from zero per cent. at W.

The next step in the construction of the model would

be to erect three plane figures on the three edges of the triangle corresponding to the three binary alloys. The sketch (Fig. 33) shows the appearance of such a space model.

If lead is then added to the binary eutectic of lead and tin the melting point of the mixture is lowered. The same effect is noticed when tin is added to the lead-tin eutectic and when bismuth is added to lead-tin. Since these three

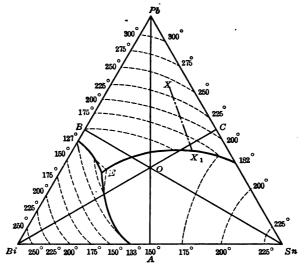


Fig. 34.—Ternary diagram with contour lines (Charpy).

lines all slope downward their intersection must lie at a point lower than the melting point of any of the binary eutectics. This point is shown at E, Fig. 31 (p. 59) and is the ternary eutectic. The shape of the space model for an alloy of this type will be apparent from the considerations just outlined. The three lines connecting the single ternary eutectic with the three binaries form the lower edges of the three valleys made by the intersections of the three curved surfaces, composing the liquidus surface.

If this surface is projected on its triangular base and

contour lines drawn, representing the intersections of a series of parallel horizontal planes with the space model a figure of the shape shown in Fig. 34 results. These contour lines, which are naturally isothermals (lines of constant temperature), show that the surfaces above the binary eutectic valleys are convex.

Consider, next, the changes which take place on cooling such an alloy as is represented by X in the diagram. the temperature falls, pure lead separates along the line X- X_1 , the relationship of bismuth and tin staying constant. At X_1 enough lead has separated so that lead and tin are in the eutectic ratio and the two metals crystallize together along the bottom of the binary eutectic valley until the composition E is reached, at which point the remaining liquid solidifies as the ternary eutectic. Although, accurately defined, a eutectic should be of constant melting point, the binary mixtures of eutectic composition vary in melting point with the amount of the third element. As a matter of easy statement, however, the mixtures of binary eutectic composition are universally referred to as binary eutectics. If a number of ternary alloys of Pb. Sn and Bi are studied and the points determined at which the binary eutectics begin to form, planes drawn through these points will give the binary eutectic This is found to consist of six twisted surfaces, each intersecting its neighbor in such a way that there will be three ridges, the binary eutectic lines, and three valleys, the projections of which connect the ternary point E with the three corners of the triangle. alloys of the series become solid at the temperature of the ternary eutectic, the solidus surface is a horizontal plane through the ternary eutectic point E.

In the actual construction of these ternary diagrams, the common practice is to study a number of vertical sections from which the space model or its projection can be assembled. In the lead-tin-bismuth series, for example, a fairly complete study of the alloys of the compositions represented by the lines Pb-A, Sn-B and Bi-C, Fig. 34, gives a general idea of the shape of the model, and the necessity for further study in the area Bi-O-B is apparent.

Referring again to Fig. 32, it will be seen that a series of alloys starting with the composition represented by X and with gradually increasing percentages of bismuth (section X-Bi) will give much additional information with regard to conditions in the eutectic area. This series might be followed by another section in which the percentage of bismuth is kept constant at 50 per cent., while lead and tin are varied. By studying several sections in this way it is soon possible to construct the space model accurately.

Microscopic Appearance of Ternary Alloys.—The microscopic study of these alloys is not satisfactory. The primary crystals are perfectly normal but the binary eutectic separations occur so slowly and over so considerable a temperature range that segregation generally takes place and the normal eutectic structure is lost. The ternary eutectic is, also, so finely divided and so intimate a mixture that the component elements can be found only by careful double etching and then with much difficulty. That three distinct structure elements are present, however, is shown in the photograph, Fig. 35.

In the class of technically important ternary alloys are included Babbitt metal and nickel silver (formerly called German silver). The composition of Babbitt metal varies over a considerable range but it is usually an alloy of tin, antimony and copper. A common composition is tin, 90 per cent., antimony, 7 per cent. and copper, 3 per cent. Microscopic examination shows the alloy to consist of crystals of SbSn and Cu₃Sn imbedded in a tin matrix. Babbitt metal is an antifriction alloy and because of its comparatively low

tensile strength is commonly used to line bronze bushings, the bronze giving the needed strength and the Babbitt the low frictional resistance. The microscope is of great use in the making of Babbitt lined bearings as by its aid it is possible to detect segregation in the metal and also to determine the size of the SbSn crystals. Large crystals, due to very slow cooling when the Babbitt is cast, and excessively fine crystals, due to a sudden chilling of the molten metal, both produce unsatisfactory bearing

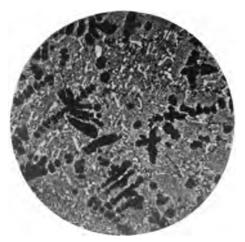


Fig. 35.—Ternary diagram of lead, tin and bismuth. 75 × (Homerberg).

surfaces. A temperature of approximately 100°C. for the mould has been found to give satisfactory results.

Nickel silver is composed of copper, nickel and zinc. It has a wide use in the production of non-corrodible articles, table ware (with or without silver plating), and the like.

Alloys with four or more constituents are not uncommon. Some of them find important application in the manufacture of easily melted fuse plugs for automatic sprinkler systems. Wood's metal corresponds to the

ternary eutectic of Bi, Pb and Sn to which a small amount of cadmium is added. It melts at 70°C.

The Phase Rule. This chapter on equilibrium diagrams would not be complete without reference to the Phase Rule which, while it is of little use to the technical metallographist, has been a most valuable tool in the study of equilibrium diagrams, making it possible to state in any given case what the equilibrium conditions actually are. Knowing the conditions which should exist at equilibrium, the microscope makes it possible to decide at once whether or not equilibrium has been reached.

The general statement of the phase rule is as follows:

$$F = C + 2 - P$$

in which F represents the number of degrees of freedom, C the number of components and P the number of phases. In the general case these factors are often difficult to define but in the application to metallic alloys no such difficulty is met. The components, C, are obviously the The degrees of freedom are the changes which the alloy can undergo, namely, changes of temperature, concentration and pressure. Since vapor can be neglected with most alloys and since the pressures commonly met in alloy practice are too small to have any appreciable effect, changes in pressure can be omitted, reducing the variables (degrees of freedom) to temperature and concentration. A phase is defined as a homogeneous. physically distinct substance. In dealing with alloys, it may be a pure metal, a metallic compound or a solid solution. In addition, each physical state of the substance, whether solid, liquid or gas constitutes a separate phase.

Neglecting the vapor phase and the effect of pressure,

¹ FINDLEY, "The Phase Rule and Its Applications."

the Phase Rule for alloys may be reduced to the simple form

$$F = C + 1 - P$$

The number of components in a binary alloy is 2, so the expression is still further simplified and takes the form

$$F = 3 - P$$

A concrete illustration of the use of the Phase Rule is given in the following diagram, Fig. 36. A point at

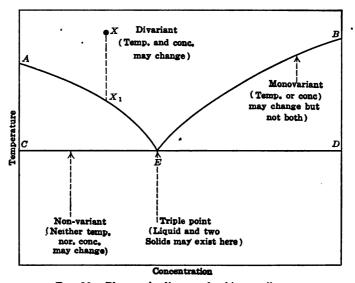


Fig. 36.—Phase rule diagram for binary alloys.

X lies in the liquid phase. Substituting 1 in the simplified expression it becomes, F=3-1=2. In words, the alloy now possesses two degrees of freedom. Both temperature and composition can be varied within the area bounded by AEB and the alloy will stay molten. This field then represents an area of divariant equilibrium. At the point X_1 on the line AE, the crystal is beginning to separate but is in contact with the liquid. Two phases, crystal and liquid, are present and the expression becomes,

F = 3 - 2 = 1. The alloy, now, has only one degree of freedom, for any change in temperature is accompanied by a change in concentration along the line AE, and a change in concentration necessitates a change in tempera-The lines AE and BE are therefore lines of monovariant equilibrium. At the point E, the eutectic point, or at any other point on the eutectic line, CED, two crystal phases, A and B, are in contact with a liquid phase of composition E. (Solid E contains A and B in the form of very fine crystals.) Under these conditions, the expression becomes F = 3 - 3 and the system becomes non-variant. Neither the temperature of the mixture nor the composition of the three phases can change until one of the three phases has disappeared. The temperature cannot fall until all the liquid phase, E has solidified nor can it rise without the disappearance of either A or B. It must not be understood that the mixture can have only the composition represented by the It may have any composition along the line point E. CD but, in this case, the composition of each phase remains the same, the difference in original composition producing changes in the relative amounts of the three. The line CD, therefore, is a line of non-variant equilibrium.

One of the principle uses of the Phase Rule is to determine whether or not true equilibrium has been reached. It is evident that, since an alloy with less than zero degrees of freedom is an impossibility, there can never be more than two crystal phases in contact with, or separating from, a two component liquid metal. Therefore, in a case like that indicated in Fig. 26, p. 53, and illustrated in Fig. 28, p. 55, the presence of three phases, in the microscopic section of the solid alloy, is a positive indication of incomplete equilibrium.

CHAPTER IV

THE NON-FERROUS ALLOYS OF TECHNICAL IMPORTANCE

No attempt will be made to describe or even to name the large and constantly increasing number of nonferrous alloys used in practice. Certain of them are of such great technical interest and importance, however, that their properties must be considered. Many have been referred to in connection with the equilibrium diagrams and others are of such special character that their consideration is out of place here. The majority of the important non-ferrous alloys not yet discussed fall into one of two groups; the smaller, containing aluminum and its alloys, the larger, the alloys of copper, particularly the brasses and bronzes.

Aluminum Alloys.—While the commercial development of the alloys of aluminum has produced many alloys of light specific gravity coupled with valuable mechanical properties, it has also very great possibilities for investigation, notably along the lines of alloying the aluminum base with two or more other metals. Pure aluminum, as cast, has a tensile strength of about 14,000 pounds per square inch, but by cold work, as in wire drawing, this may be increased to nearly 50,000 pounds. The commonest casting alloy is that with a composition of 92 per cent. aluminum and 8 per cent. copper which has a tensile strength of about 20,000 pounds but is more readily corroded than aluminum itself.

The most valuable alloy is that known as **Duralumin**, which is aluminum containing from 3.5 per cent. to 5.5 per cent. copper, 0.5 per cent. to 0.8 per cent. manganese and

about 0.5 per cent. magnesium. It has several remarkable properties and is the only aluminum alloy which has been successfully heat treated. As cast, the alloy has a tensile strength of about 35,000 pounds per square inch and an elongation of 17 per cent. in two inches. it is heated to 400°-500°C. and then quenched, there is no great change in the physical properties. If, however, the quenched alloy is allowed to "age" for a few days, the tensile strength will increase to about 58,000 pounds and the elongation to 23 per cent. By hard rolling, duralumin may have its tensile strength increased to 85.-000 pounds per square inch. In sheets, tubes and similar articles it breaks at about 50,000 pounds. Weight for weight, duralumin is as strong as the best steel and for the same strength has greater rigidity. Unlike other aluminum alloys containing copper it is markedly resistant to corrosion and compares favorably with copper under similar conditions. The properties of duralumin make it a most useful alloy for the construction of various articles especially in airplane and motor parts.1

The preparation of aluminum alloys for metallographic examination presents some difficulties. The preliminary polishing should always be done on emery papers moistened with oil and the final polishing cloths must never be allowed to dry. Liquid abrasives are absolutely necessary for successful results. The structure of the polished alloys is developed by immersion in dilute hydrofluoric acid followed by treatment with nitric acid. For detail work a 0.10 per cent. solution of sodium hydroxide in 50 per cent. alcohol is recommended.

Copper and Its Alloys.—Enormous quantities of pure copper are used in the electrical industry because of its

¹ An excellent discussion of aluminum alloys is given by Merica, Chem. and Met. Eng., 19 (1918), 135 and Bull. 76, Bureau of Standards, April. 1919.

very high conductivity. Copperforms solid solutions with many of the common elements, including practically all of those with which it is associated in its production from the ore. A fact of great technical importance is the remarkable effect of the existence of solid solutions on the conductivity of an alloy. If the alloy is of the eutectic type, the elements are completely insoluble in each other in the solid state and the conductivity of the solid alloy is practically the sum of the conductivities

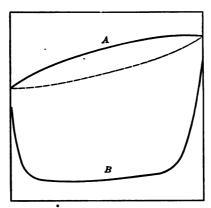


Fig. 37.—Relation between solid solution and electrical conductivity. A is the equilibrium curve and B the curve of conductivity.

of the component metals. When solid solutions occur, the conductivity drops off very sharply, the corresponding curve taking the form of a steep sided U as in Fig. 37, in which A is the equilibrium curve and B the curve of conductivity corresponding to it. The rapid decrease in conduction due to slight addition of the dissolving element makes evident the harmful effects of even small percentages of dissolved impurities on the conductivity of the copper and the necessity of accurate analysis if the metal is to be used for electrical work. Oxygen dissolves in copper to an appreciable extent and also unites with it to form cuprous oxide, Cu_2O . The com-

pound then reacts with the copper to form a eutectic series of alloys with a eutectic at 3.5 per cent. Cu₂O (0.39 per cent. oxygen). Since the presence of this eutectic has a harmful effect both on the electrical and mechanical properties of copper, all high grade copper is deoxidized in the process of manufacture. This may be done by the use of phosphorus, silicon, boron and probably, other readily oxidized elements. Deoxidizing by means of silicon in the form of copper silicide gives copper with high conductivity. Boron is highly effective as a deoxidizer and boronized copper is not infrequently specified for electrical work.

For general industrial purposes, copper is used in the form of rolled sheets, tubes, bars and drawn wires. These mechanical operations have such marked effects not only on the physical but on the metallographic properties of copper that they will be considered in some detail. Copper as cast has a tensile strength of from 17,000 to 20,000 pounds per square inch and its ductility is indicated by an elongation of from 40 to 50 per cent. in two inches. It is possible by simple mechanical work, such as rolling or drawing, to increase the tensile strength to almost 50,000 pounds per square inch. This increase in tensile strength is accompanied by a great increase in hardness and a marked decrease in elongation. Hard brass wire may have an elongation of only 1 or 2 per cent.

Several theories have been proposed to account for this phenomenon of hardening by means of mechanical work, a phenomenon which is by no means confined to pure copper but is a general property of metals and alloys. The most logical theory and the one which gives the most adequate explanation of the known facts is known

¹ For a description of the mechanical testing of alloys and of the effects of work see ROSENHAIN, "Physical Metallurgy," Chapter XI.

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as the amorphous cement theory which was proposed by Beilby and has been carefully studied by Rosenhain



Fig. 38A.—Moderately worked Muntz metal (Cu 60 %-Zn 40 %). $75 \times .$ (O'Daly.)

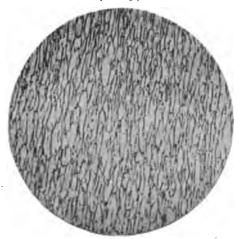
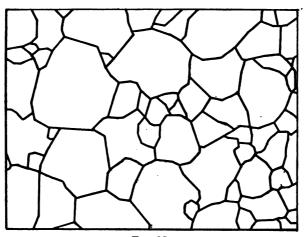


Fig. 38B.—Specimen A after hard drawing.

and his associates. This theory, now generally accepted, assumes that when a metal is subjected to such an amount of strain, either tensile or compressive, that its

elastic limit is exceeded, the crystals become elongated not by a simple stretching of the material but by a slipping taking place along certain of the crystal planes.



"Frg. 39.

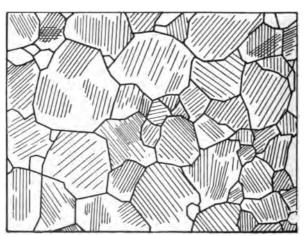


Fig. 40.

That the elongation of the crystals is very marked under certain conditions is shown in the photomicrographs, Figs. 38, A and B. The changes taking place within the

crystal are shown in Figs. 39 and 40 sketched from Rosenhain's photographs which represent a piece of soft iron before and after straining. The dark lines crossing the crystals in Fig. 40 are due to the fact that the surface is no longer plane but is covered with a large number of

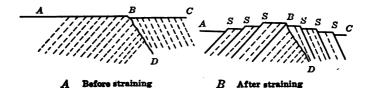


Fig. 41.—Sketch showing the way in which slip bands are produced in strained metal. (Rosenhain.)

microscopic ridges formed by the displacement of many crystal layers. These dark lines, or bands, are called *slip bands* and are characteristic of overstrained metal (see also Fig. 48, p. 87). The sketches, Figs. 41 and 42, illus-

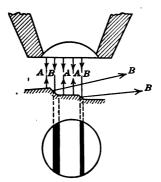


Fig. 42.—Sketch showing the optical reason for the appearance of slip bands.

(After Rosenhain.)

trate the probable nature of slipping and the optical reason for the dark slip bands. Rays "A" (Fig. 42) striking the horizontal surfaces are reflected back into the eyepiece and produce light bands. Rays "B" strike the oblique surfaces, are reflected out of the field and cause the black

lines or bands. Granting that slipping does occur along crystal planes, it is easy to believe that the rubbing of the surfaces wholly destroys the crystalline character of an extremely thin layer of the metal, producing what has been called an amorphous cement or amorphous binding material between the displaced layers. Since it may be assumed that the slipping would first occur along those planes where the crystalline cohesion was least, it would naturally follow that a greater tension would need to be applied to cause additional elongation. This fact, together with the belief that the amorphous material is both harder and stronger than the crystalline form, would account for the increased hardness and tensile strength of material which has been subjected to mechanical work. As the amorphous material has no planes along which slipping can take place to relieve an imposed strain, it follows that a sudden shock is apt to cause it to fracture. The same fact limits the amount of mechanical work which can be done on a metal before it becomes necessary to cause a partial recrystallization of the amorphous material by annealing. The annealing of metals having an excessive amount of amorphous material has the function of decreasing the brittleness and reducing the strain hardness.

Etching of Copper Alloys.—The most effective reagent for alloys rich in copper is ammoniacal hydrogen peroxide. For ordinary brasses containing 70 per cent. copper and 30 per cent. zinc the proportions should be approximately one part of 3 per cent. hydrogen peroxide to five parts of strong ammonia (sp. gr. 0.90). The amount of hydrogen peroxide must be increased with higher percentages of copper and decreased as the copper decreases. The ratio of peroxide to ammonia should be about 1 to 10 for use with alloys of the Muntz metal type (Cu 60 per cent., Zn 40 per cent.). The reagent does not keep and it is

essential for success that it should be prepared immediately before use. The mixture is applied to the polished surface by swabbing with cotton soaked in the liquid, after which the surface is washed in running water and again treated for a few seconds with the etching reagent. Alternate treatments with alkaline peroxide and water will soon develop the crystal structure in such a way that the finest details become visible. This method of etching requires a little experience but the results will be found to repay any time spent in practice with it. Dark, overetched surfaces are commonly due to excess of ammonium hydroxide, while surfaces lacking in detail are usually caused by too much peroxide although this lack of contrast may be due to severe overstrain. α -brass (p. 82) is colored buff or brown by the mixture while β -brass (p. 82) is generally yellow.

Ammonium persulphate, $(NH_4)_2S_2O_8$, in strong ammonia (1 gr. per 20 c.c.) is often used to identify β -brass which it attacks more readily than it does α -brass.

Nitric acid (sp. gr. 1.20) is used for rapid development of the crystal structure. The resulting etched surface shows strong contrast but the details are not so sharply defined as with the peroxide and the alloy is not so satisfactory to photograph.

Ferric chloride solution (p. 32) is effective for use with arsenical brass.

Bronze. Copper-tin.—The equilibrium diagram of the copper-tin alloys is very complex as Fig. 43 shows, consisting of one definitely established compound Cu₂Sn and five solid solutions in which it is probable that the compounds CuSn, Cu₅Sn₂, Cu₄Sn and Cu₅Sn exist, although this fact has not been fully established.

The important tin bronzes are practically all included in that section of the diagram in which the percentage of tin is less than 30 per cent. or, in other words, the desirable properties are associated with the α and β crystals. Four classes of bronzes are of importance.

1. Coinage bronze containing 96 to 92 per cent. copper is used largely in the production of "copper" coins and medals, the small amount of tin present increasing the hardness and wearing qualities of the copper.

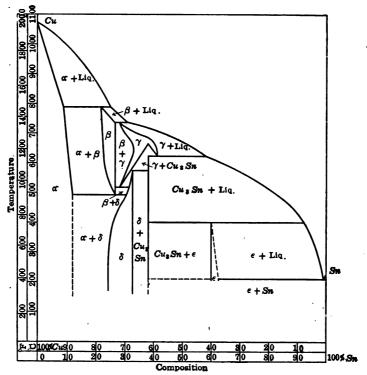


Fig. 43.—Copper-tin diagram.

2. Gun metal and gear bronze vary in composition from 92 to 88 per cent. copper. Gun metal is no longer used in the manufacture of ordnance but is often used where strong, heavy castings are to be made. In order to increase the fluidity of the metal and make the casting operation simpler, a small amount of zinc is frequently

added. A standard alloy of this class has the composition 88 per cent. copper, 10 per cent. tin and 2 per cent. zinc. This is usually known as Government Bronze, "G" Metal or simply "88, 10 and 2." It has a fairly high tensile strength, 32-38,000 pounds per square inch, and is often used where pressures, steam or hydraulic, are to be met, or for bearings subject to heavy loads.

Another bronze of the same class consists of 89 per cent. Cu and 11 per cent. Sn and is very generally used, under the name of English gear bronze in the manufacture of heavy gears. A brilliant, mirror surface is developed at the contact between the teeth of the gear and the driving mechanism and an excellent bearing and wearing surface results.

3. Bearing Bronzes.—These alloys vary from 87 to 81 per cent. copper and usually contain one or more elements in addition to the tin. The best example of this class is the bearing bronze to which phosphorus (in the form of phosphor copper) and lead have been added. These alloys, called phosphor bronzes, are of two classes, those to which phosphorus is added only as a deoxidizer and those in which an excess is present to act as a hardener. In the first class the function of the phosphorus is simply to increase the strength and ductility of the alloy by removing the Cu₂O eutectic and other oxides. In many cases, in spite of the marked improvement in physical properties, the actual amount of phosphorus is negligible. In the second class, the phosphorus, even though present in small quantities, usually less than 1 per cent., forms extremely hard particles of Cu₂P, too brittle in themselves to be used in a bearing but forming and excellent non-abrasive skeleton in the strong, tough bronze matrix. Lead is frequently added to bronze in small amounts and, as it is an insoluble constituent, is found fairly uniformly distributed throughout the metal

in the form of drops, Fig. 44, A. Lead gives to the metal two valuable characteristics. It makes it more easily



A. Unetched bronze showing lead drops.



B. Etched to show dendritic structure. Fig. 44.—Phosphor bronze with 4 per cent. of lead. 75×.

machined and, to a certain extent, self lubricating because of the soft, greasy character of the suspended

- lead. The lead drops are sources of weakness in an otherwise strong metal so that the amount of lead must be carefully adjusted to fit the conditions under which the bearing is to be used. For most purposes the lead content is less than 2 per cent., although in the plastic bronze, previously mentioned (p. 9), it may reach 50 per cent.
- 4. Bell Metals.—These alloys contain from 80 to 75 per cent. copper and are of especial interest because they must be worked either at a temperature above dull redness or the hot metal must be suddenly chilled (quenched) and then worked cold. Reference to the diagram (Fig. 43) will show that work is done in both cases on the β -solid solution. In the first case, the work is done while the alloy is in the β -temperature range and, in the second case, the sudden chill retains the bronze in the condition in which it existed at the higher temperature (see p. 57). With the increase in tin to more than 25 per cent., the brittleness becomes so great that the alloys are handled only with difficulty and are used exclusively for decorative purposes where the material is not subjected to strain or shock.

Brass.—The copper-zinc alloys are the most important of the copper alloys because they are relatively inexpensive as compared to tin bronze. The diagram for the brasses is, like that of the bronzes, very complex, consisting of six series of solid solutions which probably contain, as in the other case, definite compounds (Fig. 45).

The γ -solid solution, which begins to be formed when the percentage of zinc is increased above 50 per cent., probably contains the compound Cu₂Zn₂ and is so brittle that alloys in which it occurs are practically valueless except for decorative purposes where strength and ductility are not required. This limits the technically important brasses to three classes: α -brass, from 0 to 36

per cent. zinc; $\alpha + \beta$ -brass, from 36 to about 42 per cent. zinc; and β -brass, from 42 to about 50 per cent. zinc, at which point the tensile strength and ductility both drop to nearly zero. The following curves show the relationships between tensile strength properties and metallographic constitution of cast copper-zinc alloys (Fig. 46).

It will be seen that the strength of cast brass increases from about 28,000 pounds per square inch with pure copper to more than 60,000 pounds per square inch with

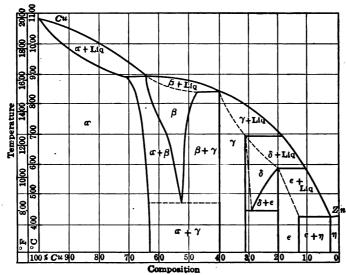


Fig. 45.—Copper-zinc diagram. (Shepard.)

45 per cent. zinc (pure β), so that by choosing the composition, any desired strength within these limits may be obtained. It must be clearly understood, at this point, that the figures just given are not absolute, but relative, as the physical properties vary within fairly wide limits, even with cast material, depending on various factors such as the shape of the cast piece, the material of which the mould is made and the rate at which the metal cools.

The actual number of commercial brasses is very great but, for convenience, they may be grouped in a few classes. The cost decreases with the increase in the percentage of zinc so that very high copper alloys are not much used.

1. Gilding Metal or Jewelry Brass.—This contains from 1 to 20 per cent. zinc and is used under various trade names in the manufacture of cheap jewelry. The color of some of the alloys in the group is not unlike that of standard gold.

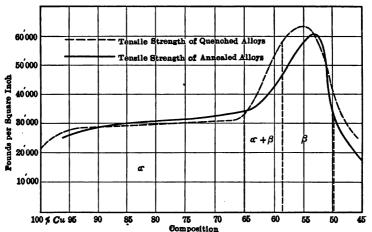


Fig. 46.—Relation between chemical composition of copper-zinc alloys and tensile strength. (After Johnson—J. Inst. Metals, xx, 233.)

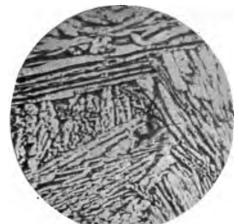
- 2. Dutch Metal.—These alloys contain between 20 and 25 per cent. zinc, are very malleable and are used largely in the hammered form as substitutes for gold leaf.
- 3. Brass for Cold Working.—The group in which the zinc varies from 27 to 35 per cent. includes by far the larger number of the technically important brasses. This range of compositions lies at the zinc rich end of the α -brass field and, therefore, includes the alloys of high tensile strength coupled with maximum ductility. In

this class are found the alloys used for sheet metal, tubes, wire, cartridge cases and other articles which are to be subjected to severe mechanical work.

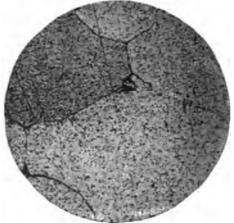
4. Muntz metal and similar alloys contain from 37 to 45 per cent. zinc and include the α and β - and the pure β -brasses. Pure β -brass does not exist in copper-zinc alloys which have been cooled slowly from a high temperature but may be obtained as a perfectly homogeneous solid solution by quenching an alloy with 60 per cent. copper from a temperature of 800°C. Owing to the fact that normally cooled alloys of the Muntz metal type are composed of two components, α and β , they are usually worked hot so that the metal may be in its homogeneous condition. Pure β -brass shows little or no tendency to twin even after it has been worked and annealed. It is colored yellow by NH₄OH and H₂O₂ and may be distinguished in this way from α -brass which under similar treatment becomes distinctly brown. mixture of NH4OH and ammonium persulphate is often successfully used in the examination of Muntz metal as the β -brass is colored yellow while the α -brass is practically unaffected by a short treatment with this reagent. The characteristic appearance of α -brass in a ground-mass of untwinned β -brass is shown in the following photographs, Fig. 47, A, B, C, and D, the differences in the size of the α -masses being due to differences in heat treatment and chemical composition.

Alloys of the Muntz metal type are fairly resistant to corrosion by salt water if the α and β crystals are small and intimately mixed. They are used to a considerable extent in the sheathing of wooden ships, for condenser tubes and for other purposes where the lesser ductility is not a serious objection. Because of the cheapness of zinc the Muntz metal alloys are sometimes substituted for the more expensive α -brass. These

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A. Cast Muntz metal (150×).



B. Muntz metal annealed at 750° and quenched. Chiefly β -brass. $75 \times$. (Johnson and Jermain.)



C. Munts metal annealed at 750° and cooled in air. 75×. (Johnson and Jermain.)



D. Muntz metal annealed at 750° and cooled in furnace. Shows brown islands of α -brass in a matrix of β -brass. $75 \times$. (Johnson and Jermain.)

Fig. 47.—Muntz metal.

alloys may be made much less readily corroded by the addition of about 1 per cent. tin as in Naval Brass.

- 5. Brass Solder.—For brazing iron, the solder contains 35 per cent. of zinc while, for soldering brass, the alloy of 50 per cent. is most commonly used.
- 6. White Brass.—When the percentage of zinc is more than 50, the resulting alloys become increasingly light in color and are very brittle. These alloys are known as the white brasses and are used only for ornamental castings.
- a-Brass.—The most important single alloy is that whose composition is very near 70 per cent. copper and 30 per cent. zinc. It possesses great ductility, about 56 per cent. elongation and a tensile strength when cast of 30,000 to 35,000 pounds per square inch, a strength which is greatly increased by mechanical work.

One of the most important uses of this "70-30" brass is in the production of shell or cartridge cases which, in the process of manufacture, are subjected to severe mechanical work. Practically all brass shell cases from those used for the small revolver to the large cases used in naval guns are made by a series of punching and drawing operations. As was stated on p. 72, this working produces an elongation of the crystal grains and a marked hardening and increase in brittleness of the metal. following photograph, Fig. 48, is of interest in showing the value of metallographic as well as chemical control of cold-worked brass. The chemical analysis is excellent but the strain has been enough to produce great distortion of the crystal grains and the production of numerous slip bands. This strained condition can be wholly relieved by suitable annealing. The striking feature of cold-worked α -brass which has been annealed is the production of twin crystals characterized by alternate dark and light bands (Fig. 50, C). These twins may be so small

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as to be scarcely visible at a magnification of seventy-five diameters or they may be so large that with the same



Fig. 48.—Badly strained α -brass showing distorted crystals and many slip bands. 75 \times .



Fig. 49.—Cartridge brass as cast. 75 X.

n agnification a single crystal may cover the entire field of vision of the microscope. These differences in crystal

size are shown in Figs. 49 and 50A, B, C, D, which are all α -brasses of the same chemical composition (70 per cent. copper and 30 per cent. zinc), but differ in the amount of mechanical and heat treatment. Although it may be said in a general way that the higher the annealing temperature the larger the crystal grains, other conditions being equal, it is also true that the crystal size depends on the amount of cold work to which the brass has been subjected. This means that for each sample of cold-worked brass there is an annealing temperature which will produce crystals of the desired size, this temberature depending on the extent to which the brass has been deformed by mechanical work. Fine crystal grains indicate increased tensile strength and hardness with decreased ductility while large crystals are always accompanied by softness, lower tensile strength and greater ductility.

This connection between crystal size and physical properties has led to the introduction of definite grain size requirements in many specifications, not only for brass and bronze but also for steel. A convenient means of studying grain size has been proposed by Jeffries2 and is recommended by the American Association for Testing The method consists in projecting the mag-Materials. nified image of the specimen onto a ground glass plate on which has been inscribed a circle 79.8 millimeters in diameter (area = 5000 sq. mm.). The ground glass is placed with its ground surface toward the specimen and on the outer, smooth surface the number of whole crystals included in the circle is counted. This may be done conveniently by checking each crystal with a soft (glass) pencil. The number of grains intersecting the circum-

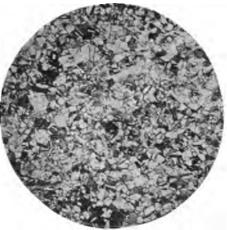
¹ MATHEWSON and PHILLIPS, Am. Inst. Min. Eng., Feb., 1916.

² ZAY JEFFRIES, "Grain Size Measurements," Met. and. Chem. Engr., vol. xviii, p. 185.

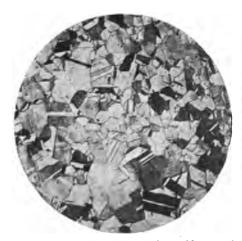
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A. Severely cold worked cartridge metal beginning to recrystallize. 75 ×.



B. Cold worked and annealed. Small twin crystals are visible. 75×.



C. Moderately cold worked cartridge metal after annealing. 75 ×. (The characteristic twinned structure is very marked.)



D. Moderately cold worked cartridge brass annealed at 700° C. 75×. (Large twin crystals due to overheating.)

Fig. 50.—Brass—70 % copper, 30 % zinc.

ference of the circle is then counted and 0.5 of this number, added to the number completely included in the circle, gives a close approximation to the total number of crystals present. To obtain the number of grains per square millimeter, the crystal count is multiplied by a factor which depends on the magnification used. The standard magnifications, as recommended by the American Society for Testing Materials, are, for steels, 50-100-250 and 500 diameters and for non-ferrous alloys, 25-75-150 and 250 diameters. The multiplying factors are given in the following table.

Diameter of circle in milli- meters	Magnification used	Multiplying factor to obtain grains per square millimeter
79.8	10	0.020
79.8	25	0.125
79.8	50	0.500
79.8	75	1.125.
7 9.8	100	2.000
79.8	150	4.500
79.8	250	12.500
79.8	500	50.000

If the grain size is to be expressed as the average diameter of the crystal in millimeters, or its area in μ^2 , the following formulas from Jeffries paper will be found useful:

z =completely included grains;

w = boundary grains;

x= equivalent number of whole grains in 5000 sq. mm. (circle 79.8 mm. in diameter or rectangle with area of 5000 sq. mm.); $x=\frac{1}{2}\dot{w}+z$.

m = magnification;

f =multiplying factor used to obtain grains per

square millimeter (see table);
$$f = \frac{m^2}{5000}$$

 $n = \text{number of grains per sq. mm.}; n = fx$
 $d = \text{diameter of average grain in mm.}; d = \frac{1}{\sqrt{n}}$
 $a = \text{area of average grain in } \mu^2$. $a = \frac{1,000,000}{n}$

One of the most serious defects in worked brasses and bronzes is the strained condition leading to the formation of what are known as season cracks. Various articles of cold worked brass may be so badly strained and so imperfectly annealed, that storage for a period of from several weeks to a number of months, particularly in a moist climate, leads to a spontaneous break down of the strained metal and the production of large or small season cracks. It happens, frequently, that this dangerous condition is not at all apparent even on careful inspection. Because of its comparative frequency, it has become the custom in many instances to insist on a test for season cracking with a specified number of samples from an entire lot. This can be done effectively by immersion of the suspected sample for 4 hours, in a 1½ per cent. solution of mercuric chloride or mercuric The season cracking phenomenon is greatly accelerated by this treatment and the tendency to crack at once disclosed.

It is essential that α -brass which is to be exposed to severe mechanical treatment should be free from bismuth, antimony, iron and lead as all are sources of weakness. For brass which receives only a moderate treatment, small percentages of iron or lead will not be dangerous. Iron gives to the alloy increased strength coupled with increased hardness and decreased ductility, while lead acts, as it does with bronze, to reduce the

tensile strength but to make the brass far more readily machined. Bismuth and antimony tend to form brittle envelopes around the α -crystals and to destroy the ductility that makes cold work possible.

For special purposes, small percentages of other elements are added to the brass alloys. The use of lead has been mentioned as improving the machining qualities though reducing the tensile strength, but only when the percentage of lead is very low (less than 0.5 per cent.) can the brasses be worked hot. Tin. when added in small quantities increases the hardness of brass but causes a marked decrease in ductility. When added to 70-30 brass in amounts from 1 to 1.5 per cent., an alloy which is very resistant to sea water. Admiralty metal, is formed. The addition of manganese in amounts less than 4 per cent., gives to the brasses very desirable properties. It is usually added to brasses of the Muntz metal type, together with small amounts of tin, iron and An alloy of this general type, called, unfortunately, manganese bronze when it should be manganese brass, is much used in making propeller blades, rudders, ship fittings exposed to sea water, and for other engineering purposes requiring a strong, non-corrodible alloy. Aluminum, when added in very small amounts. increases the fluidity of molten brass to a marked degree, rendering the casting operation easier and producing cleaner castings. It materially increases the strength of the brass but rapidly reduces its ductility so that the amount added should never exceed 3 per cent.

Aluminum Bronze.—Another technical copper alloy of great importance is the alloy with aluminum known as aluminum bronze. The diagram, Fig. 51, is not unlike the tin-bronze and brass diagrams in its general character and complexity. The only alloys of technical importance, however, lie in the α -field (copper solid

solution varying from 0 to about 11 per cent. aluminum) and, at the opposite side, in the η field, which is a series of solid solutions of copper in aluminum, saturated at about 10 per cent. copper. The light alloys of aluminum with copper have already been mentioned, p. 69. The alloys in the α -field have remarkable physical properties, the addition of aluminum causing a striking increase in tensile strength. In castings, for example, while 30 per

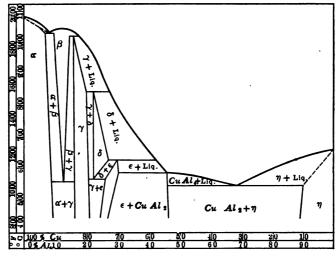


Fig. 51.—Aluminum bronze diagram. (Carpenter and Edwards, Gwyer, Curry.)

cent. zinc gives a brass with a tensile strength of about 30,000 pounds per square inch and 10 per cent. tin will give a bronze with about 40,000 pounds tensile strength, the addition of 10 per cent. aluminum to copper gives an aluminum bronze with a strength of about 70,000 pounds per square inch. Its elongation is about 20 per cent., nearly as great as that of brass and twice as much as that of tin-bronze and the alloy is considerably harder than either. Aluminum bronze is used in the manufacture of castings requiring strength and toughness, and is espe-

cially resistant to shock or to alternating stresses. It has the added advantage that it is from 10 to 15 per cent. lighter than the corresponding brasses and tin bronzes. This alloy would be more extensively used if it were not for certain difficulties in its manufacture which are apt to cause lack of uniformity in the finished product. Properly made aluminum bronze is a very valuable alloy.¹

¹ Extended discussion of the technical non-ferrous alloys will be found in Law, "Alloys and Their Industrial Applications;" Gulliver, "Metallic Alloys;" Desch, "Metallography." References to current practice will be found in the "Institute of Metals" (British) and in the "American Institute of Metals" which has recently become affiliated with the "Institute of Mining Engineers."

CHAPTER V

IRON AND STEEL

The most important applications of metallography, as well as the most difficult, lie in the uses, defects and methods of heat treatment of iron and steel. culties of the study of this series of iron-carbon alloys may be traced to various causes, among them the fact that in the technical study we are dealing, even in what are known as the "plain carbon" steels, not with a simple alloy of iron and carbon but with an exceedingly complex mixture of iron, carbon, phosphorus, manganese, sulphur and silicon. While the effects of the last four elements, when they are present in small quantities, as is usually the case, are not comparable with the effects produced by comparatively slight changes in carbon content, no one of the constituents can be wholly neg-Increase in any one of them, above a certain wellrecognized maximum, causes far-reaching changes in the physical and metallographic properties of the metal. When elements like chromium, nickel, vanadium or tungsten are added in making the alloy steels (self hardening, high speed tool steel, etc.), the situation becomes so complex that little is known from an equilibrium standpoint. An enormous amount of work is yet to be done in systematizing the present knowledge of the properties of the alloy steels.

A second factor which complicates the exact study of the iron-carbon diagram is that the iron exists in various allotropic forms, each one of which has different physical properties, notably magnetic properties and each one of

which varies in its ability to dissolve carbon. During the cooling of chemically pure iron (electro-deposited) five or six holds in the curve have been noted by various investigators but, because of uncertainties as to the possible effects of dissolved gases, it is generally assumed that iron exists in three allotropic forms: (1) γ -iron, stable above 900° and practically nonmagnetic; (2) β-iron, existing between 780° and 900°; and (3) a-iron, stable below 780° and strongly magnetic. The changes just indicated occur on cooling the iron and, from the initial of the French word, "refroidessement," are often referred to as the Ar₃, Ar₂ and Ar₁ points, respectively. The changes take place at slightly higher temperatures on heating and, in abbreviation of the word, "chauffage," are often called the Ac₃, Ac₂ and Ac₁ points. They are also called critical points or transformation points. As the percentage of carbon is increased the Ar₃, Ac₃, Ar₂ and Ac, are progressively lowered until at the temperature of 780° to 790°C, and with the carbon content increased to 0.85 per cent, the three critical points coincide. The temperature range which includes all the critical points is called the critical range and is of great importance in the annealing of steel. This temperature range extends from about 800° to 900° with low carbon steels. decreases to an interval of 10° (from 780°-790°C.) at the composition 0.85 per cent. carbon and then increases from this point as the carbon content increases.

A third complication in the iron-carbon system is due to the fact that many of the reactions involved occur in the solid state and therefore, unless the alloys cool with extreme slowness, the changes take place

¹A group of English metallographists question the existence of β -iron and consider only the α and γ forms. The great majority of metallographists, however, still agree that thermal evidence warrants belief in the β -form.

incompletely or not at all. It is also true that in the higher carbon range, from 4.3 per cent. C upward, the equilibrium relationships have never been satisfactorily settled.

The enumeration of these various difficulties might lead to the impression that a study of the metallography of iron and steel is a hopeless task. This is far from true as many of the difficulties have been overcome and the study has been carried on along so many lines that information of the utmost value to the makers and users of iron and steel has been obtained. It is also true that so much remains to be done that there is an unlimited field of investigation for those who have the opportunity and the inclination to carry on the work.

It is beyond the scope of this book, nor is it its purpose, to consider except in a general way the various branches of the metallography of iron and steel. For detailed information the reader is referred to one of the larger books dealing solely with this side of the subject.

Classification of the Iron Carbon Alloys.—Dealing first with that group of alloys consisting chiefly of iron with varying amounts of carbon, the metals are divided into three groups, depending on the carbon content and method of manufacture; (1) wrought iron, (2) steel and (3) pig or cast iron.

Wrought iron contains normally less than 0.3 per cent. carbon and is prepared by melting the crude pig iron, as it comes from the smelting furnace, with hematite (iron oxide). The resulting pasty mass is first hammered and then rolled to remove from it most of its impurities. The chief foreign substance is an iron silicate slag which is never wholly removed by the squeezing of the rolls but becomes elongated, giving to wrought iron its characteristic fibrous structure, Fig. 52.

¹ SAUVEUR, "Metallography and Heat Treatment of Iron and Steel."

This material has been largely replaced by the cheaper mild steel which has many of the same physical properties. Wrought iron is sometimes specified, however, because of its easy welding and its resistance to shock.

Steel includes the alloys having less than 1.7 per cent. carbon and the properties of this group of alloys is sub-



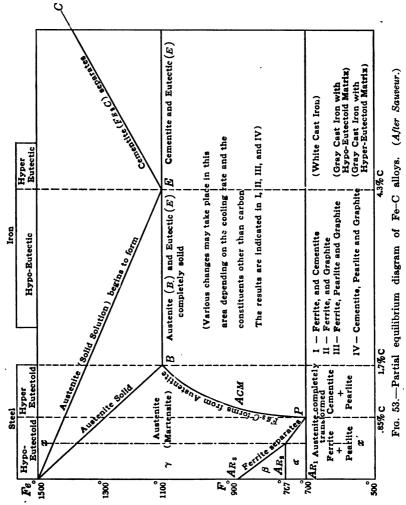
Fig. 52.-Wrought iron.

ject to the widest variation, depending on the method of production, the rate of cooling, the subsequent heat treatment and other factors.

The term iron includes the alloys from 1.7 per cent. carbon upward, usually not in excess of 4 or 5 per cent.

The Equilibrium Diagrams.—Many metallographists have studied the alloys of iron and carbon in the greatest detail and have proposed new equilibrium diagrams or

have suggested modifications of the first one. Though differing somewhat from it in special points, all of them,



with the exception of the Upton diagram, resemble in general outline the early diagram of Roberts-Austen.

¹ UPTON, J. Phys. Chem., 12 (1908), 506.

² ROBERTS-AUSTEN, Proc. Inst. Mech. Eng., 1899, 35.

This is especially true of the alloys in the steel range (less than 1.7 per cent. C). Much more uncertainty exists in the range of the irons, largely, no doubt, because the lesser importance of this group has not warranted the immense amount of study that has been given to steel.

A simplified and probably incomplete iron-carbon diagram is given in Fig. 53 from which most of the important general relationships can be studied. diagram is a combination of eutectic (p. 11), solid solution (p. 39), compound (p. 49) and eutectoid (p. 57). The valuable properties of steel depend to a large extent on the fact that, as is always true of reactions in the solid state, the decomposition of the solid solution γ into its components requires time and can be prevented almost wholly by a sufficiently sudden cooling. It is evident from the diagram that pure iron never separates from a liquid solution of carbon in iron but that the solid which first separates along the line FeE is a solid solution of carbon in iron becoming a saturated solution when 1.7 per cent. carbon has been added. Referring to the diagram, it will be seen that all steels are originally solid solutions of carbon in iron, the carbon content varying from almost zero up to the saturation point, 1.7 per cent. The eutectic E is a mixture of the solid solution B and the solid which separates along the line EC. Whether the solid separating on this line is actually the definite compound (Fe₃C) is open to question and will be considered later.

Decomposition of the solid solution γ takes place along the lines FP and BP which intersect at the eutectoid point P. FP is a line along which pure iron separates and BP represents the separation of the definite compound Fe₃C.

Consider, now, the changes which take place when a

steel containing 0.5 per cent. carbon cools from the molten state to ordinary temperatures as indicated by the line xx' in Fig. 53. At x the metal is liquid. When the line FeE is reached a solid solution begins to separate and at the temperature represented by the intersection of xx' with FeB the steel has wholly solidified. Throughout the area FeFPB, the alloy is a solid solution, possibly of carbon in iron, but, more probably, of the compound Fe₃C in iron. Along the line FP a change in the solid state takes place with a separation of pure iron and, as a result, a change in the concentration of remaining solid solution until it contains about 0.85 per cent. carbon and has reached a temperature of from 680° to 700°. At this temperature and composition the final change in the solid solution takes place with the formation of the eutectoid P, an intimate mixture of the pure iron and the compound Fe₃C. Steels containing less carbon than that corresponding to the eutectoid (0.85 per cent. C) are known as hypo-eutectoid steels while those from 0.85 to 1.7 per cent. C are the hyper-eutectoid steels. In this latter range the solid solution decomposes along the line BP with the separation of the compound Fe₃C. reducing the carbon content until the eutectoid point P is again reached, when the same eutectoid mixture as before is formed. When complete equilibrium has been established, hypo-eutectoid steels consist of varying amounts of pure iron imbedded in the eutectoid P, while the hyper-eutectoid steels are mixtures of Fe₃C with the same eutectoid. At P, only the eutectoid will be found.

Incomplete Transformations.—If the behavior of steel on rapid cooling was as simple as has just been indicated there would be only three classes of steels, (1) mixtures of iron and the eutectoid, (2) the eutectoid itself and (3) mixtures of Fe₃C and the eutectoid. Thus

the physical properties of the steel could be readily determined by a knowledge of the physical properties of the three substances involved. It is, however, rarely the case in practice that complete equilibrium is established. so that by far the larger number of technical steels represent imperfect equilibria due to incomplete transformations along the lines indicated in the diagram. Extremely rapid cooling, such as quenching from a high temperature in liquid air, produces the unchanged solid solution; while either very slow cooling or annealing for a considerable time at a temperature just below the eutectoid temperature, will give the eutectoid mixture. Between these extremes are various intermediate transition forms with varying physical properties. Several of these intermediate substances have such characteristic microscopic structure and definite physical properties that they have been named as a means of distinguishing them from each other. These names are not at all descriptive but have a certain historical interest as they are based on the names of men who have been leaders in the development of the science of metallography. decomposed y-solid solution is called Austenite, after Roberts-Austen, one of the pioneers in the metallography of steel. Following this is the more usual component found in quenched steel, Martensite, after the German metallographist Martens; next Troostite, from the French chemist Troost; Sorbite, after Sorby, and finally Pearlite, resembling mother of pearl, the only product of which the name is at all descriptive. The transition briefly stated is from Austenite -> Martensite -> Troostite -> Sorbite -> Pearlite. To complete the naming of the common constituents of steels, the pure iron separating along the line FP has been called Ferrite and the compound Fe₃C. Cementite, as it is the important constituent of those steels which have been hardened by the cementation

process. It is hardly necessary to say that the changes are not as abrupt as the limited series of names might indicate but that there are still other intermediate products to which such combination names as troosto-sorbite and sorbitic-pearlite have been given. The name Osmondite, from Osmond the French metallographist who was a pioneer in the microscopic study of steel, is sometimes given to the product at the exact boundary between troostite and sorbite but is not frequently used

Etching of Steel and the Microscopic Appearance of Its Constituents.—Many etching reagents have been suggested, some of them extremely complex mixtures, but for most purposes three or four different solutions will be found sufficient.

Nitric Acid and Alcohol.—The most commonly used reagent is a solution containing 4 c.c. of concentrated nitric acid (sp. gr. 1.42) in 96 centimeters of ethyl alcohol. This is used by immersing the specimen for about 10 seconds and agitating the liquid constantly to prevent the retention of gas bubbles on the polished surface. After treatment, the specimen is washed thoroughly in running water and dried either by patting gently with soft linen or cotton, or by means of a blast of air.

Picric Acid.—For low carbon steels a solution of 5 grams of picric acid in 95 c.c. of alcohol is frequently used.

Alcoholic Hydrochloric Acid.—Martens and Heyn recommend the use of a solution containing 1 part of hydrochloric acid (sp. gr. 1.19) in each 100 parts of alcohol. The reagent acts much more slowly than alcoholic nitric acid, requiring about one minute, but the results are excellent.

Special Reagents. Copper Ammonium Chloride.—For examination of the specimen without the microscope (macroscopic examination), and, especially, for the pur-

pose of locating segregated areas in large specimens, a solution of 8 parts of copper ammonium chloride in 100 parts of water is used. This reagent is suitable only for plain carbon steels and must be applied by immersing the specimen.

Iodine Solution.—A solution containing 6 parts of iodine in 100 parts of alcohol is used for macroscopic examination and is applied by swabbing the polished surface with cotton soaked in the solution. The operation is continued for five minutes, a fresh portion of reagent being added as soon as the iodine color produced by the preceding treatment has disappeared. The iodine reagent must be prepared immediately before use. It is effective in showing excessive slag, phosphorus segregations and other irregularities.

Kourbatoff's Reagent for Cementite.—Cementite is not affected by the usual reagents but is colored black or brown by immersion from three to five minutes in a boiling solution of sodium picrate in sodium hydroxide. The reagent contains 2 parts of sodium picrate in 98 parts of a 25 per cent. solution of sodium hydroxide. Ferrite is unaffected by this reagent so that Kourbatoff's mixture furnishes a sure means of distinguishing between these two components.

Time Required for Etching.—With all these reagents the time required varies somewhat with the nature of the steel under examination. If pearlite requires 10 seconds immersion, as it will with alcoholic nitric acid, sorbite will need 7 or 8 seconds, martensite about 5 seconds and troostite, which is most sensitive to chemical reaction, will take only 2 or 3 seconds for the development of its structure.

Occurrence and Physical Properties of the Constituents of Steel. General.—In dealing with slowly cooled steels in complete equilibrium it is only necessary

to consider the physical properties of the three possible constituents, (1) ferrite, (2) pearlite, and (3) cementite. These are shown in the following table (Sauveur).

Constituents	Tensile strength in younds per square inch	Elongation, per cent. in 2 inches	Hardness
Ferrite	About 50,000	40 ±	Soft
Pearlite	About 125,000	10 ±	Hard
Cementite	5000 (?)	0	Very hard and brittle

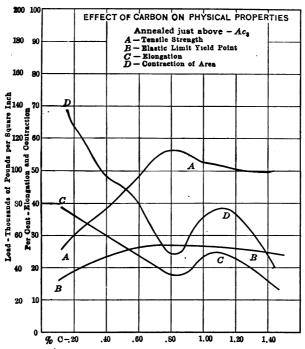


Fig. 54.—Diagram showing effect of carbon. (After J. H. Nead, Am. Inst. Min. Eng. (1916), 2341.)

As every annealed steel is a mixture of two of these three constituents, it is to be expected that the physical properties can be fairly closely predicted from the chemical composition. The tensile strength, for example, increases from about 50,000 pounds per square inch with pure iron, to 125,000 pounds per square inch with pearlite (0.85 per cent. C), and then decreases as the amount of cementite increases. In the same way the ductility, as represented by the percentage elongation, decreases from that of pure iron and becomes very low indeed

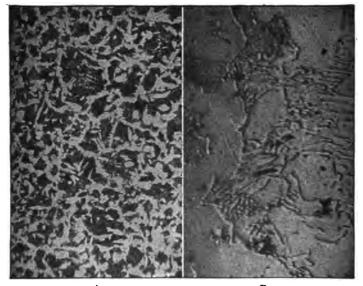


Fig. 55.—Pearlite and ferrite. $A = 123 \times .$ $B = 1650 \times .$

when the carbon content is more than 1.20 per cent owing to the increase in brittle cementite. These general relations of pearlitic (fully annealed) steels are shown in the sketch, Fig. 54, and the microscopic appearance is given in Figs. 55 and 56. The former illustrates a hypo-eutectoid steel, the latter is typical of the hyper-eutectoid class. The thumb print structure in each case is the eutectoid pearlite. By heat-

ing pearlitic steels for a number of hours at 600°-700° the laminated structure gradually disappears, due to the coagulation of the layers of cementite in the eutectoid, with the formation of spherical masses. This operation is known as spheroidizing and the cementite as spheroidized cementite.

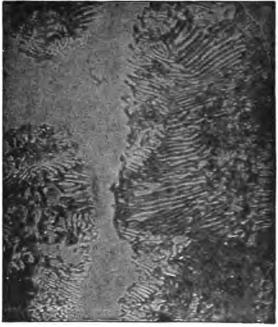


Fig. 56.—Cementite and pearlite 1650×. (The white mass is cementite and the dark eutectoid pearlite.)

The slowly cooled (pearlitic) steels have many industrial uses. Very low carbon steel, or extra mild steel, containing less than 0.1 per cent. C is used for articles which must be readily worked like rivets or horseshoe nails and is also used for material which is to be subjected to cementation (see p. 117). Low carbon, or mild steel, with carbon up to 0.25 per cent. may be

used for screws, bolts, agricultural implements, sheets, wire and structural steels, though much of this material, due to treatment in the process of manufacture, is not strictly pearlitic. Steels containing from 0.25 per cent. to about 0.60 per cent. carbon form the class usually known as medium high carbon or half hard steel. As the carbon content increases the use of completely pearlitic steel is decreased. Wholly or partially pearlitic steels in this range are used for castings, shafting, piston rods and cylinders for compressed gas.

When the carbon is from 0.6 to 0.85 per cent., the steels are classed as high carbon or hard steels and among the many uses may be mentioned tires, springs, cheap cutlery, wire, certain agricultural tools and wood working tools. Practically no steels in the range from 0.85 to 1.25 per cent. carbon are used without some heat treatment which will modify the pearlitic character to a greater or less degree.

Rapidly Cooled and Tempered Steels.—The changes which take place when a steel is quickly cooled (quenched) and subjected to a later heating (tempering or annealing) are so numerous that only a few can be considered as illustrating the general character of the resulting proper-The first metallographic constituent of chilled steel which might be expected is austenite (Fig. 57), but it decomposes so quickly on cooling that it is never formed in the commercial hardening of plain carbon steel. It is the chief constituent of certain alloy steels, however. and will be considered later (p. 113). The constituent commonly produced when steel is quenched is martensite (Fig. 58), the first transition product of the decomposition of austenite. This substance is extremely hard, brittle and unworkable so that pure martensitic steel is rarely found in practice. Associated with other constituents such as troostite or free ferrite, in low carbon steels, and with cementite, in the high carbon steels, it is always found in hardened tool steels in amounts which vary with the method of its production. The quenching of an edged tool may be taken as a single example of the production of martensite. The tip only of the tool is heated to redness and dipped in water. The brittleness of the resulting martensite is reduced, with a consequent sacrifice of hardness, by allowing heat to flow from the unquenched portion of the tool



Fig. 57.—Austenite and martensite. (The dark masses are martensite and the light ground mass austenite.) 350×.

to the tip, until the desired softening results, when the entire tool is quenched and the final product has the combined properties of chilled and tempered steel.

The decomposition which takes place in the tool just described, after it has been subjected to partial quenching, leads to the formation of troostite (Fig. 59). As troostite is a decomposition product of martensite, it is to be expected that in its physical properties it will differ from martensite in decreased hardness and increased ductility. Its hardness is about halfway between that of

martensitic and pearlitic steel of the same carbon content. The tempering of troostite leads to a rapid increase in duc-



Fig. 58.—Martensite. 900 X.

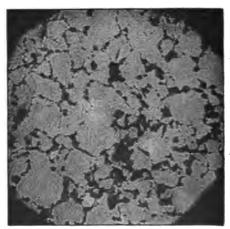


Fig. 59.—Martensite and troostite. 117 X.

tility with a decrease in hardness. It may be formed by cooling slowly through the transformation interval, as for example when small pieces of steel are quenched in oil, but it is much more frequently produced by reheating (tempering) a chilled steel below 400°. It is a constituent of practically all plain carbon steels, which have been hardened (tools for example) and is associated in varying amounts with martensite, depending on the temperature of tempering. When great hardness is required and brittleness is of less importance, as in the production of razor blades for instance, a temperature of about 200° is used, producing relatively small amounts of troostite. When toughness as well as hardness is re-

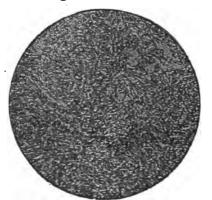


Fig. 60.—Sorbite. $350 \times$.

quired, the amount of troostite is increased by tempering at 300° to 400°. Most tools are tempered between 200° and 300°.

While it is almost never the custom in practice to temper above 400° it is, perhaps, easier to correlate the physical properties of *sorbite* (Fig. 60) with those of troostite by considering the former as produced by the tempering of troostitic steels in the range from 400° to 600°. Sorbitic steels are softer and more ductile than troostitic and not as soft as pearlitic steels. Sorbite, like troostite, is one of the decomposition products of austenite and is, in fact, imperfectly formed pearlite.

It may be produced by heating a chilled steel in the range between 400° and 650° but it is usually made by regulating the cooling rate in such a way that, while the chilling action is not great enough to produce martensite, it is too rapid to allow the complete formation of pearlite. It may be formed (1) by cooling small pieces in air, (2) by quenching larger pieces in oil from a temperature just above the critical range or (3) by quenching small pieces in water from a point near the bottom of the critical range. Though slightly less ductile than pearlitic, sorbitic steel has so high a tensile strength and elastic limit that it is used for the highest grade of structural work. It is not possible to give absolute values to the physical properties of sorbite as its character varies so much with the method of production. It may be stated for purposes of comparison that while sorbite sometimes reaches a tensile strength of 140,000 pounds per square inch, ordinary pearlite will have a strength of about 110,000 pounds per square inch while the coarsely laminated form of pearlite will show a tensile strength of only about 70,000 pounds per square inch.

The following table from H. C. Boynton gives the relative hardness of the different constituents of steel as compared with ferrite (pure iron) as a standard. It must be remembered that these values, particularly for the intermediate forms like sorbite and troostite are only approximations.

Ferrite = 1
Pearlite = 43
Sorbite = 52
Troostite = 88
Austenite = 104
Martensite = 239
Cementite = 272

Alloy Steels.—In addition to the elements silicon, phosphorus, manganese and sulphur, always found in small quantities in carbon steels, other elements are often added to make the ternary or quaternary alloy steels, many of which have remarkable physical properties. The subject of alloy steels is so large and the information concerning them changing so rapidly that only a very general discussion can be given here in spite of the great and constantly increasing importance of these alloys. A few general principles seem to hold, though even these must not be accepted as absolutely established but rather as suggestive.

- 1. If the carbon content is kept constant, the addition of the alloying element in increasing amounts causes the steel to be first pearlitic, then martensitic and finally, with a sufficiently high percentage of the third element, to become austenitic.
- 2. By holding the percentage of the alloying element constant and increasing the carbon content the changes under similar cooling conditions are, as before, from pearlitic, to martensitic, to austenitic steel.
- 3. It follows, almost as a corollary to (1) and (2), that the higher the carbon content the less the amount of alloying element needed to complete the structural change and, conversely, the higher the percentage of alloying element the less carbon is needed to change the structure and properties. These changes are shown graphically in the diagram (Fig. 61).

The number of known alloy steels is great and constantly increasing. Among the commoner ternary steels are those containing either nickel, manganese, tungsten, chromium, vanadium, molybdenum or silicon, in addition to the carbon. In the quaternary class may be found chrome-nickel, chrome-tungsten, chrome-vanadium, nickel-vanadium and others. Other and still more

complex series are the chrome-nickel-vanadium, chrome-tungsten-vanadium and the like. A detailed discussion of these alloys is impossible and only a few will be considered to illustrate in a general way the properties of each group.

The strictly metallic elements like manganese, nickel and chromium lower the critical points of steel very decidedly so that austenite and martensite can be formed much more easily than is the case with carbon steel. A steel containing from 1 to 1.5 per cent. carbon and

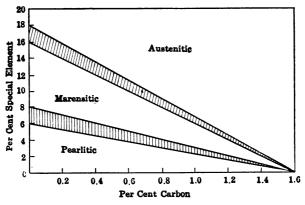


Fig. 61.—Constitutional diagram of alloy steels. (Sauveur after Guillet.)

from 10 to 15 per cent. manganese can be obtained easily in the austenitic condition by reheating the cast steel to about 1000°C. and quenching in water or oil. The resulting steel is hard and resistant to wear but, at the same time, possesses much ductility. It has been used in making rails subjected to excessive wear, as on sharp curves.

The less metallic alloying elements, like tungsten, vanadium and molybdenum have little or no effect on the critical points (p. 96) but, due to the formation of double carbides, tend strongly toward the production of cementitic steels.

If manganese is added to a tungsten steel, the alloy first formed on cooling is of the cementite class. If, however, this steel is reheated to a high temperature and cooled in the air, the carbide which is dissolved at the high temperature is retained in the martensitic condition. Such a steel is said to be "self hardening."

One of the most important of the alloy steels is the chrome-tungsten or high speed tool steel. Such an alloy, with from 10 to 20 per cent. tungsten and 2 to 10 per cent. chromium, has the characteristics of cementite when slowly cooled. On reheating to a very high temperature, often almost to the melting point of the steel, the carbide dissolves and, if the cooling is fairly rapid, the steel retains an austenitic or martensitic structure with corresponding physical properties, notably great hardness. The striking fact in this case, however, is that the martensite formed in this way shows no tendency to soften even at relatively high temperatures, approaching 600°C. This makes it possible to run a cutting tool at such speed that, while its edge will become visibly red, it will still retain its hardness, a property absolutely impossible with common carbon steel. These illustrations will serve to show some of the possibilities of alloy steels.

Heat Treatment of Steel. 1—The most important property of steel is the power which it has of changing its physical condition under the influence of heat. Many of the changes have been considered in connection with the discussion of the various metallographic constituents: sudden cooling or quenching, for example, produces the hard martensite; tempering hardened steel softens it, producing troostite or the still softer constituent sorbite. Annealing may be carried out for one of three reasons; (1) to increase the softness and

1 BULLENS, "Steel and Its Heat Treatment," Ed. 2.

ductility, (2) to relieve the strains produced by chilling or by mechanical work, or (3) to reduce the grain size. The second object has been considered in the case of worked or strained brass (p. 76) to which strained steel is wholly analogous. Severely worked steel shows the same elongated structure illustrated in Fig. 38 and the restoration of its normal structure by annealing is of the same character as with brass. Improvement of the physical properties may be brought about by annealing whereby the size of the crystal grains is reduced. Large crystal grains are almost always an indication of weakness while the production of small grains invariably leads to greatly improved mechanical properties.

Temperature of Annealing.—The steel must be heated to a temperature slightly above its critical range in order to have the crystalline structure affected, and it has been found that the higher the temperature above the critical range the more coarsely crystalline the resulting steel will be. The most suitable temperature varies, of course, with the carbon content but should be approximately as follows for plain carbon steels. (American Society for Testing Materials.)

Carbon content	Annealing range	
Less than 0.12 per cent	875° to 925°C.	
0.12 to 0.25 per cent	840° to 870°C.	
0.25 to 0.49 per cent	815° to 840°C.	
0.49 to 1.00 per cent.	790° to 815°C	

After the desired temperature has been reached the object must be kept at that temperature until it is heated throughout its mass. It is then cooled either (1) in the annealing furnace, producing the softest, weakest and most ductile metal; (2) in air, giving a somewhat harder and less ductile material; or (3) by quenching in oil, giving the hardest, strongest and least ductile steel of

the three. The finest possible structure would be obtained by quenching from a point as near the critical range as possible, but, except with very low carbon content, the resulting steel would be hard and lacking in ductility. The double anneal overcomes this difficulty. The operation consists in reheating the hardened steel to about 650° (close to, but below its critical range), which serves to relieve the hardness and at the same time to retain the fine structure.

Case Hardening.—An operation closely allied to heat treatment is case hardening, a process which is carried on for the purpose of adding a hard, non-abrasive surface to a strong, ductile steel. The steel used for this purpose has a low carbon content (0.2 per cent. or less) and is carburized by heating in contact with a carbon furnishing substance, either in the solid, liquid or gaseous form. Numerous materials have been used of which charred leather, potassium ferrocyanide and barium carbonate may be considered types. As carbon dissolves very slightly in α-iron, if at all, the case hardening temperature must be above the critical range and is usually between 850° and 1000°C. The depth to which the carbon penetrates depends on the length of time during which the steel is in contact with the carbonaceous material and varies from 0.5 millimeter to 5 millimeters with an average depth of from 2 to 3 millimeters. Metallographic examination of a case-hardened specimen shows a surface coat of hard cementite over a band of eutectoid, free from cementite and ferrite, and below this band the soft interior mass or core in which ferrite largely predominates. The coarse structure of the core produced by the long heating during the case hardening process, must then be refined by suitable heat treatment.

Cementation is a similar operation applied to wrought iron for the purpose of changing it into steel. It differs

from case hardening in that the steel produced in this way is afterward melted and the carbon becomes uniformly distributed in the ingot, forming cement steel.

Cast Iron.—Reference to the iron-carbon diagram (p. 99) shows that the cast iron field extends from 1.7 to 4 or 5 per cent. C. The liquidus curve has two branches, along one of which (FeE) austenite should separate and along the other (CE) cementite. The cementite separating along CE is so readily decomposed on cooling that three classes of cast irons are commonly recognized, depending on the cooling rate and on the presence of constituents other than carbon.

1. White iron results from rapid cooling (chill casting) of the metal and has the white fracture and

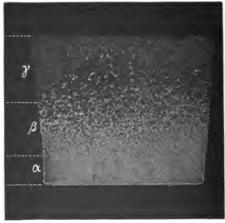


Fig. 62.—Chilled casting. (Actual size.) α layer is white iron.

hard, brittle qualities of cementite. Chill castings are too hard to machine and are seldom used in the production of small articles. It is often necessary to produce soft, fairly strong cores with extremely hard surfaces as, for example, in car wheel treads or the surfaces of rolls. In such a case the white iron (cementite)

surface may be produced by casting against a highly heat-conducting material like an iron plate. The pro-



Fig. 63.—Section made from white border, α , in Fig. 62. 350 \times .

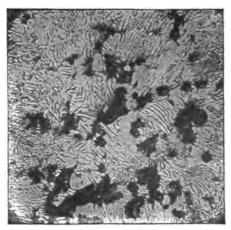


Fig. 64.—Graphic temper carbon in malleable iron. 350 x.

duction of white iron is also favored by the absence, or low percentage, of silicon and the presence of high percentages of manganese and sulphur (Figs. 62 and 63).

An important decomposition product of white iron is produced by annealing for several days at a temperature of about 730°C. Under these conditions the hard, white cementite decomposes into graphite and ferrite, the graphite separating, however, not in the massive form but as an amorphous black powder (temper carbon) (Fig. 64). This malleabilizing process produces an iron which is much stronger than gray iron of the same com-

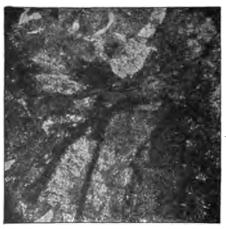


Fig. 65A.—Taken at the part γ, in Fig. 62. 350 × shows gray iron.

position. The tensile strength of malleable iron is more than 40,000 pounds per square inch as against an approximate 20,000 pounds for gray iron with the same amount of free carbon in the fibrous instead of the powdery form. Malleable iron is used for castings which are to be subjected to shock, especially in the manufacture of small castings which would be made of steel if it were not for the technical difficulties involved in steel casting.

2. Gray cast iron is produced when the cementite first formed is allowed, by decreasing the rate of cooling, to decompose into ferrite and graphite. This gives a dull

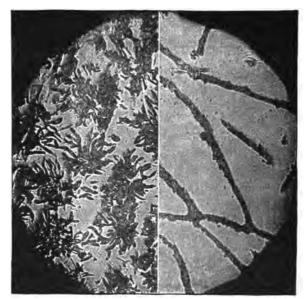


Fig. 65B.—Graphite in iron. 115×. The halves represent two specimens of iron with different carbon content.

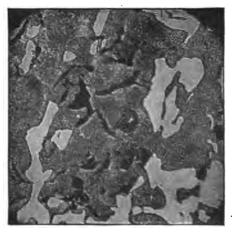


Fig. 66.—Section taken at the transition zone, β in Fig. 62 mottled iron. $350 \times \cdot$

gray appearance to the fractured metal. Under these conditions, the graphite separates in the form of long fibrous masses unaffected by etching reagents (Figs. 65a and 65b). The separation of graphite is increased by the addition of silicon which, in gray castings, is usually present in amounts varying from 2 to 4 per cent. The tensile strength of gray iron varies from 18,000 to about 23,000 pounds per square inch.

3. Mottled Iron.—By a suitable regulation of the cooling rate, an iron containing both free cementite and graphite is produced with properties depending on the relative amounts of the soft and hard constituent (Fig. 66).

CHAPTER VI

DEFECTIVE MATERIAL

Not the least important of the many uses of metallography is its application to the study of defective or unsuitable material. A distinction must be made between the terms "defective" and "unsuitable" as a perfect alloy may be wholly unsuited to the purpose for which it has been, or is to be, used. The causes of defective metal are numerous but they may generally be classified in one of four groups:

- 1. Incorrect chemical composition;
- 2. Improper mixing, melting or casting;
- 3. Unsuitable mechanical treatment;
- 4. Improper heat treatment.
- 1. Incorrect Chemical Composition.—Large errors in chemical composition produce effects which are too obvious to need more than a reference. If an alloy which was supposed to be brass with 70 per cent. copper, actually contained but 50 per cent. copper and was subjected to severe cold work the results would be disastrous. Such errors, however, are found by the analyst rather than by the metallographist.

Slight errors in chemical composition are generally far more serious because they are so much less readily detected. Not infrequently these differences in chemical composition are so localized as to escape detection by analytical processes and yet they are of far-reaching effect on the physical properties of the material. Some of these defects have been referred to, as for instance,

the formation of brittle envelopes around brass crystals when bismuth or antimony is present (p. 92). The commonest chemical defect is the presence of segregated material which is without question one of the most common causes of failure in metals. Segregated impurities occur in many technical alloys but to a far greater extent in steel and iron in which their presence may do serious harm. Until recently but little infor-

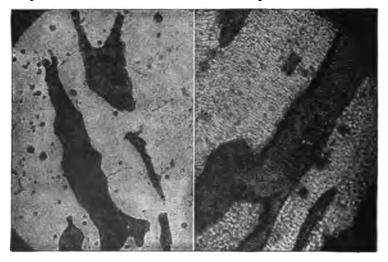


Fig. 67.—Slag inclusions in wrought iron. 350 X.

mation has been available on defects of this sort in non-ferrous metals. During the past year, however, two papers¹ have been published showing by microphotographs, inclusions of the oxides of tin and zinc as well as of casting sand and other non-metallic substances in brass and bronze.

In the case of iron and steel, chemical inclusions usu-

¹Comstock, "Non-metallic Inclusions in Brass and Bronze," J. Am. Inst. Metals, March, 1918. Carpenter & Elam, "An Investigation on Unsound Castings of Admiralty Bronze," J. Inst. Metals (British), xix, 155.

ally consist of slag (commonly silicates of iron or other elements), sulphides of iron or manganese, phosphides of iron or manganese or metallic oxides. Slag is a normal constituent of wrought iron but may at times segregate in such a way as to become harmful (Fig. 67). Small amounts of oxide and silicate are always present in steel and if the quantity is not excessive and is uni-

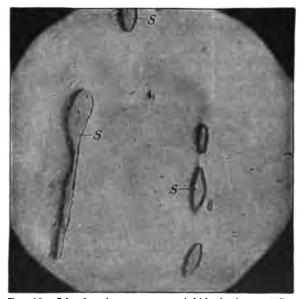


Fig. 68.—Islands of manganese sulphide in iron. 117 X.

formly distributed will not seriously effect the mechanical properties of the metal. Irregular distribution of the non-metallic material in segregated areas is always a source of danger and can be detected more readily by the metal microscope than in any other way.

Sulphides, either of manganese or iron, are sources of danger, especially in material which is to be worked hot (rolled, hammered or drawn). Manganese sulphide is sometimes found in steel rails in a form which

under the microscope resembles long, narrow islands, dove gray in color (Fig. 68). Sulphide inclusions are easily detected by the production of "sulphur prints." In the older method of Heyn this is effected by hold-



Fig. 69.—Sulphur print on silk. (Actual size.)

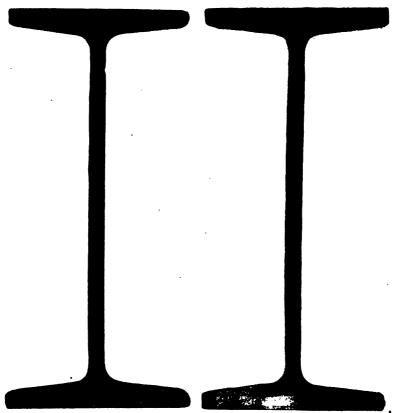
ing a piece of white silk moistened with mercuric chloride and hydrochloric acid in contact with the polished surface of the metal (Fig. 69). Black stains of mercuric sulphide are produced at the points of contact with the



Fig. 70.—Sulphur print of a defective boiler plate showing sulphide streaks.

sulphide spots. The same effect is obtained more simply by soaking photographic printing paper (Velox or Cyko) in 2 per cent. sulphuric acid and applying the paper to the polished sample. Black spots or streaks

of silver sulphide are produced. The print may be made permanent by fixing it in "hypo" (sodium thiosulphate) solution in the usual way. The presence of sulphide streaks is shown in the following photograph,



A. Rolled from the top of the B. Rolled from the bottom of the ingot.

Fig. 71.—Steel I-beams showing sulphide and phosphide segregations.

Fig. 70. That the lines are actually due to sulphide inclusions is shown by chemical analysis of the separate layers (Heyn). Layer I shows 0.067 per cent. sulphur, layer II, 0.201 per cent. and layer III, 0.240 per cent.

Phosphorus in the form of phosphide is one of the most harmful of the non-metallic inclusions in mild steel. It occurs in the ingot and if too small an amount of the ingot top is removed to eliminate the phosphide segregations, these will go through the mechanical operations of rolling, forging, etc., without coming to the surface. The result is shown in Fig. 71 and illustrates in a striking fashion the advantages of metallographic over chemical examination in cases of this sort. The streaks are due in this case to sulphide as well as to phosphide inclusions. Phosphide inclusions are the usual cause of "cold shortness."

This inclusion of non-metallic impurities in alloys has been estimated to cause more than 75 per cent. of the failures found in technical practice.

2. Improper Melting, Mixing or Casting.—Another, though less frequent, reason for defective material is imperfect mixing of the molten alloy, producing layer formation in the solid. Plastic bronzes (p. 9) sometimes fail because of imperfect mixing which causes a much greater concentration of lead in one part of the casting than in another. In the light bearing-alloys of the Babbitt metal class and in type metals containing antimony, irregular distribution of the cubical crystals of SbSn is of common occurrence and is always a cause of unsatisfactory material (Fig. 72 a and b). Segregation in brasses of the Muntz metal type is not at all infrequent and in rolled or drawn material gives rise to distinct layer formation. Fig. 73 shows α - and β -brass in adjacent streaks in a condenser tube. The α -brass may be found also in the form of islands or spots in the β -field as shown in Fig. 74 a and b. These few cases illustrate the possibilities of layer formation in alloys which are duplex in structure and have components differing in specific gravities.

3. Unsuitable Mechanical Treatment.—Work, either cold or hot, may produce bad material if improperly done.

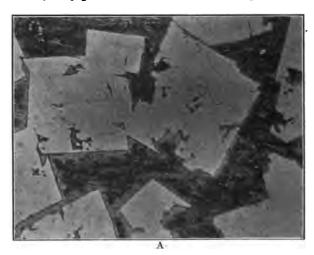




Fig. 72.—Variations in size and distribution of SbSn crystals in babbitt metal.

The effects of cold work on brass have been considered on p. 72 and illustrated in Figs. 18 and 47. The char-

acteristic fibrous structure of overworked brass is also shown in Fig. 75. Steel is more commonly worked hot and defective metal may be produced when the rolling, hammering or other operation is commenced at too high a temperature. If, for example, a steel containing ferrous sulphide (FeS) is rolled at a temperature much above 900°C. it is probable that the iron sulphide is actually molten and rolling would naturally cause serious



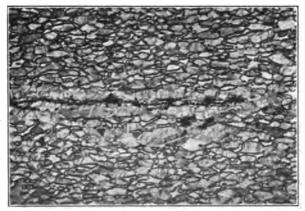
Fig. 73.—Layer formation in defective condenser tube showing α - and α + β -layers. 75 ×.

cracks in the finished material. If, on the other hand, mechanical operations are carried on (or are finished) at too low a temperature, severe strain hardening may result. Both these conditions, incipient cracking from too hot work and overstrain from cold work may be detected by the microscope. Unequal amounts of work on different parts of the same article is a frequent cause for metal failure. This produces internal strains which may ultimately lead to "season cracks" (p. 91) or may

cause immediate cracking on reannealing. Fig. 18, p. 37, shows a crack which was probably produced in this way.



A. Etched with NH₄OH and (NH₄)₂S₂O₈. α -brass very slightly attached. 75 × .



B. Part of the same tube etched with NH₄OH and H₂O₂. $75 \times$. Fig. 74.—Formation of islands of α -brass in β field.

Cold work may be done unintentionally in certain mechanical operations and may cause serious trouble.

In fitting large pieces of structural steel such as are used in bridges, building frames and the like, it is sometimes necessary to hammer the parts into position. This has been known to cause bad strain hardness in a limited area with a resulting failure of the metal. In a gas tank recently constructed a large number of rivets broke because of the overstrain produced by hammering when they were too cold. Defects produced in this way cannot, of course, be controlled by metallographic exami-



Fig. 75.— α -brass strained and not annealed. 75×.

nation but the causes of failure can often be detected by the microscope and the responsibility placed.

One other type of defective material is due to a combination of mechanical and chemical difficulties and is caused by the rolling or hammering of surface oxides or "scale" into the metal under treatment. This is one of the reasons for hard spots in rolled brass and, as it is apt to be a surface condition, it frequently leads to rapid corrosion of the material.

4. Improper Heat Treatment.—The term "heat treatment," is most commonly used in connection with heating

or cooling operations (quenching, tempering, etc.) applied to the solid alloys but, if the term is applied in a broader sense to include the rate at which a molten allov cools. it explains many cases of defective material. casting of Babbitt metal will serve to illustrate the way in which defective, or at least unsuitable, material may be produced by variations in the cooling rate of the liquid metal. Too rapid cooling produces undeveloped crystals of the tin-antimony compound SnSb, while very slow cooling causes the formation of large cubes of the compound and greatly increases the tendency of these crystals to rise to the top of the cast metal. Both conditions are responsible for unsatisfactory bearing surfaces. If the metal against which the Babbitt is poured has a temperature of approximately 100°C. the SnSb crystals will be found to be moderate in size and regularly distributed.

Heat treatment, as applied to solid alloys, consists of annealing, tempering or quenching and any one of these operations if badly executed will lead to defective or unsuitable material. The microscope is an invaluable tool in studying defects of this kind. Annealing carried on at too high a temperature may cause "burning" or "overheating." Burning is nothing but oxidation and is visible under the microscope as a marked thickening of the grain boundaries due to oxide formation. a cause of brittleness and produces fracture between the grains because of the oxide envelope with which the crystals are surrounded. Overheating is distinguished from burning in that it is not accompanied by oxidation but is a cause of excessive crystal growth. The very large crystals of overheated α -brass are shown in Fig. 50 (p. 89). In the case of steel the best physical properties are associated with fine structure so that annealing at temperatures too far above the critical range will produce material which, if it is not actually defective, is at least inferior to the steel which would be obtained by suitable treatment.

Annealing in an unsuitable atmosphere may also produce defective material. Steel, for instance, may be decarbonized and therefore materially weakened by long heating in an oxidizing atmosphere.

Tempering is carried out for the purpose of relieving strain hardness or increasing the amount of softer material at the expense of the hard material as, for example, in the change of martensite to troostite or sorbite. Tempering at too high a temperature may unduly decrease the hardness and at too low a temperature may leave an excessive amount of the harder constituent. In either case the resulting material is defective in the sense that it is not in the proper mechanical condition for the purpose to which it is to be applied.

Quenching incorrectly performed is another cause of defective or unsuitable material. Quenching from too high a temperature generally forms excessively large crystals which produce correspondingly weak metal and it may also cause a form of strain hardness which not infrequently leads to cracks. Quenching is done for the purpose of retaining the metal in the condition (usually a hard state) in which it exists at the higher temperature. If the temperature from which the metal is quenched is too low the desired hardness will not be obtained and the structure of the soft form will be seen under the microscope. Finally, if the specimen is large, the cooling rate may be unequal in different parts and local differences in hardness and strain will be produced. Warping or cracking of the quenched piece not infrequently results.

This brief discussion of some of the causes of defective material will serve to illustrate the applications of metallography to an important engineering problem and also emphasize the value of metallographic control both to the producer and to the consumer of alloys. This new branch of physical science is only one of the factors in the study of metals and, if possible, should always be used in connection with ordinary chemical analysis and mechanical testing rather than independently of them. There are times, however, when it is the only means of study that may be used without damage to the material under investigation as, for instance, in the inspection of a finished article.

In conclusion it must be said that, while metallography has become an almost indispensable science in the metal industries, the interpretation of microscopic appearances in complex cases requires a highly skilled and experienced observer. The inexperienced metallographist should be extremely careful not to overestimate the value of his observations.

APPENDIX

TABLE 1

Outline of a Brief Course in Experimental Metallography

- 1. Assemble a melting point apparatus and calibrate a thermoelement (p. 18).
- 2. Prepare a series of alloys, study the cooling curves and construct the equilibrium diagram* (p. 4). Lead-antimony, bismuth-tin and lead-tin are suggested.
- 3. Sectionalize, polish, etch and examine the alloys prepared in (2) (p. 29).
- 4. Photograph at a magnification of seventy-five diameters (75×), develop the plates, print, trim and mount the photographs (p. 34).
 - 5. If time permits study as in (2), (3) and (4) the following alloys:
 - (a) Tin-magnesium.—(Open maximum.)
 - (b) Copper-antimony.—(Open maximum and concealed maximum.)
 - (c) Tin-antimony.—(Several series of solid solutions, probably with a compound.)
 - 6. Experiments with Brass.—Polish, etch and examine (p. 29).
 - (a) Cast brass.
 - (b) Cold-worked α-brass.—(Examples of this material occur in spring brass, sheets, condenser tubes, cartridge cases and similar articles.)
 - (c) Examine severely cold-worked α-brass. Anneal for ten minutes at 550°C. and reëxamine.
 - (d) Anneal samples of cold-worked α -brass for ten minutes each at the temperatures 450°, 550°, 650°, 750° and 850° and compare the resulting crystals with reference to size.
 - (e) Examine cast Muntz metal (60 per cent. Cu-40 per cent. Zn).
 - (f) Examine extruded or hot-worked Muntz metal.
 - (g) Anneal several specimens of hot-worked Muntz metal at 800° and
- * If but a limited time is available, the number of mixtures may be divided among the members of the class so that each will make but one or two melts. The results are then collected and arranged in the form of the complete diagram.

- (1) Quench in cold water (β -brass).
- (2) Cool in air.
- (3) Cool slowly in the annealing furnace. Anneal a quenched specimen one-half hour at 400° and compare with (1).
- 7. Examination of Bronze.—(a) Examine cast bronze and compare its structure with manganese bronze and aluminum bronze.
 - (b) Examine cold-worked bronze and anneal to restore normal structure.
 - (c) Examine leaded phosphor-bronze after polishing and before and after etching. (The unetched specimen will show the distribution of lead.)
- 8. Experiments with Steel.—(a) Examine cast steel with about 0.3 per cent. carbon. Anneal for one hour at 875° and compare grain size with that of the original sample. (Etch with HNO₃, p. 103.)
 - (b) Heat specimens of steel containing approximately 0.1 per cent., 0.3 per cent., 0.6 per cent. and 0.9 per cent. C and cool very slowly through the critical range or heat for 30 minutes just below the critical range. (Note the relative quantities of ferrite and pearlite.) Examine at 100× and 500 ×.
 - (c) Quench a small specimen with about 1.2 per cent. C from 1200° (Martensite).
 - (d) Quench a small specimen with about 0.8 per cent. C from 1000° and reheat to 600° (Sorbite).
 - (e) Quench steel used in (d) as before and reheat to 350° (Troostite). Examine at $100 \times$ and $500 \times$.
 - (f) Polish two specimens of normally cooled high carbon steel (about 1.4 per cent. C). Etch one piece with nitric acid, the other with sodium picrate (p. 104). Examine at 100× and 500 × (Cementite).
 - (g) Quench a specimen with at least 1 per cent. manganese and about 1.5 per cent. carbon from 1400° in ice water (Austenite).
 - (h) Examine high-speed tool steel. Heat for twenty minutes between 500° and 600° and reëxamine after slow cooling.
 - (i) Heat a sample of steel containing less than 0.2 per cent. carbon in a mixture of 60 per cent. charcoal and 40 per cent. barium carbonate for at least two hours at 1000°. Cool and examine the entire cross section (case hardening). Note the thickness of the cementite layer.
 - (j) Select two pieces of steel with 0.5 per cent. C. Heat one to

900°, the other to 1200°. Cool both in air and examine with special reference to size of the crystal grains.

Experiments with Iron.—(a) Wrought Iron.—Polish, etch with alcoholic HNO₃ and examine wrought iron using one longitudinal and one transverse section. Note especially the color and distribution of the slag.

- (b) Gray Cast Iron.—Polish a high-silicon, high-carbon iron and examine without etching (Graphite).
- (c) White Cast Iron.—Examine a high-manganese, low-silicon iron which has been chill cast.
- (d) Malleable Iron.—Examine malleable iron etched and unetched. Note the small rounded masses of graphite due to the decomposition of cementite and compare these with the graphite plates or needles in (b).
- (e) Mottled Iron.—Examine the transition stage which will be found between the outer case and inner core of a chilled casting.

Mechanical Testing.—If testing machines are available a study of the various mechanical properties as hardness, tensile strength, elastic limit, elongation, etc. should be made with some of the commoner industrial alloys, brass, the different bronzes, steel, iron and the like and the results obtained studied in connection with the metallographic examination.

The outline just given is merely suggestive and the number of experiments may well be increased by the study of defective material as, for example, broken rails or axles, corroded boiler or condenser tubes, overheated steel or any of the cases of the same sort that may especially interest the experimenter. The field for investigation and research is unlimited.

Table 2

Books and Journals.—(This list is not complete but includes the publications most readily obtainable). The asterisk * indicates the books especially recommended for the general reader.

General

- Alliages Métalliques—Cavalier—1909.—General metallography dealing extensively with physical and mechanical properties.
- Die binären Metallegierungen—Bornemann—1909.—Brief theoretical discussion and many equilibrium diagrams.
- Einführung in die Metallographie—Goerens—1906, *Translation—Introduction to Metallography—Ibbotson—1908.—A small general metallography but a classic in that it is the first book to deal with equilibrium diagrams as well as microphotography.
- Étude Industrielle des Alliages Métalliques—Guillet—1906—General study of industrial alloys with many microphotographs.
- Etude Théorique des Alliages Métalliques—Guillet—1904—Discussion of the methods of alloy study; hardness, conductivity, magnetism, density, etc.
- Handbuch der Metallographie—Guertler—1912–1914.—The most complete and detailed treatment of metallography yet published. Much emphasis is laid on theoretical considerations.
- * Introduction to Physical Metallurgy—Rosenhain—1917.—Deals especially with mechanical testing, physical properties and industrial applications of alloys. Summary of defective material.
- Lehrbuch der Metallographie—Tammann—1914.—Deals with the subject almost wholly from the theoretical viewpoint. Contains an extended discussion of the valence theory as related to intermetallic compounds.
- *Metallic Alloys—Gulliver—1913.—One of the standard books on general metallography. Considers crystallography and the mechanism of crystallization of metals. Excellent treatment of ternary alloys.
- Metallographie—Heyn and Bauer—1909.—Small general metallography largely theoretical.
- Metallographie—Ruer—1907 (Translated by Mathewson).—Elements of metallography considered chiefly from the theoretical side.
- * Metallography—Desch—1913.—General metallography with special emphasis on physico-chemical principles and an extended

discussion of the connection between constitution and physical properties.

Metallography—Hiorns—1902—An introduction to the microscopic study of alloys.

Physikalische Chemie der Metalle—Schenk—1909.—Six lectures on applications of physical chemistry to metallography.

Traité de Metallographie—Robin—1912.—A large work on general metallography including many subjects not usually considered. A complete set of diagrams and many microphotographs.

Traite Complet D'Analyse Chimique—Goerens and Robin—1911 Métallographie Microscopique.—General metallography with many diagrams and microphotographs.

Intermetadic Compounds

- Chemical Combinations Among Metals—Giua—1918 (Translated by Robinson).—Theoretical treatment of the nature and properties of intermetallic compounds.
- Intermetallic Compounds—Desch—1914.—A monograph dealing with the constitution and physical properties (hardness, conductivity, etc.) of intermetallic compounds.

Industrial Alloys (Non-ferrous)

- Alloys—Sexton—1909.—Deals with the physical and mechanical properties of the non-ferrous alloys and the methods of preparation.
- Alloys and Their Industrial Applications—Law—1914.—A book designed primarily for the engineer with a brief theoretical discussion and a detailed description of the mechanical properties of technical alloys.
- Mixed Metals—Hiorns—1912.—A descriptive text-book on the composition, methods of manufacture and technical uses of non-ferrous alloys with a brief theoretical treatment.
- Practical Alloying—Buchanan—1910.—A description of foundry practice with alloy formulas. Essentially a foundryman's handbook.

Iron and Steel

*Cast Iron in the Light of Recent Research—Hatfield—1912.—An extended discussion of the properties of cast iron with many microphotographs. Deals with shrinkage, casting temperature, growth, etc.

- Crystallization of Iron and Steel—Mellor—1905.—Six lectures on the applications of metallography in engineering.
- Die praktische Nutzanwendung der Prüfung des Eisens mit Hilfe des Mikroskopes—Preuss—1913.—A brief discussion of the use of the microscope in the study of good and of defective steel and iron.
- Iron, Steel and Other Alloys—Howe—1903.—One of the earlier classics on the metallography of iron and steel by the dean of American metallographists.
- Metallographie und Warmebehandlung—Hanemann—1915.—A discussion of applied metallography and heat treatment of steel, designed for engineers.
- *The Metallography and Heat Treatment of Iron and Steel—Sauveur—1916.—A detailed treatment of the metallography of iron and steel with many excellent microphotographs. One of the modern standard works on iron and steel
- The Metallography of Steel and Cast Iron—Howe—1916.—A large book dealing with many theories of the behavior of iron and steel and especially with the mechanism of plastic deformation. Highly speculative and of interest to the advanced student.
- *Microscopic Examination of Steel—Fay—1917.—Intended for inspectors of steel ordnance materials. A very brief discussion of methods and many microphotographs of good and of defective material.
- The Microscopic Analysis of Metals—Osmond—1913 (Translated by Stead).—An English edition of Osmond's classic in the field of the microphotography of steel and iron. Includes many of Osmond's remarkable photographs of good and of defective material.
- * Physico-chemical Properties of Steel—Edwards—1916.—A discussion of the chemical and structural constitution of steel and the effects of heat treatment based on the equilibrium diagram.
- The Sampling and Analysis of Iron and Steel—Bauer and Deiss—1912 (Translated by Hall and Williams).—Part I deals with the applications of metallography to the selection of suitable samples for analysis.

Heat Treatment of Steel

Heat Treatment of Tool Steel—Brearly—1916.—Essentially a book for the tool maker but gives many applications of metallography. Steel and Its Heat Treatment—Bullens—1917.—A detailed discus-

sion of the heat treatment of steel and the uses of the microscope in following the changes involved.

Traitements Thermiques des Produits Métallurgiques—Guillet—1909—A discussion of the methods and results of quenching, tempering and annealing of alloys, chiefly iron and steel.

Journals

- American Institute of Metals—1906-1918 (Incorporated with Am. Inst. of Min. Eng., 1919).—Deals with the production and metallography of non-ferrous alloys.
- American Institute of Mining Engineers.—Includes the metallography of iron and steel and since Jan., 1919 has published the non-ferrous metallography formerly printed in Am. Inst. of Metals.
- American Society for Testing Materials—1899 to date.—In the metals section has published much information on the physical properties and metallography of alloys.
- Bureau of Standards, United States.—Publishes frequent valuable monographs on various branches of metallography.
- Journal of the Iron and Steel Institute (British)—1896 to date.— Deals with the preparation and metallography of iron and steel. Published semi-annually.
- Journal of the Institute of Metals (British)—1909 to date.—A semiannual publication of the Society which covers for non-ferrous alloys the field occupied by the Iron and Steel Inst. in the steel industry.
- Mitteilungen aus dem Eisenhüttenschen Instituts Aachen—Wust—1906 to date.—A series of valuable contributions to theoretical and industrial metallography.
- Zeitschrift für Metallographie.—Published original articles in English, French, Italian and German and included abstracts of all metallographic articles.

In addition to the journals devoted primarily to the properties of metals the following journals frequently publish important articles on metallography.

Chemical and Metallurgical Engineering, Metallurgie, Revue de Métallurgie, Stahl und Eisen, Zeitschrift für anorganische Chemie.

TABLE 3

The Common Industrial Alloys.—The composition of these alloys varies between fairly wide limits with a corresponding variation in physical properties and applications.

The information given under the heading "Uses" is intended merely to indicate the general nature of the alloy.

¹ Name	Per cent. composition	Uses
Admiralty metal	Cu 70 Zn 29 Sn 1	Condenser tubes for use with salt water. Marine fittings.
Aluminum brass		Propeller blades, rudder frames, sea valves.
Bronze,		
	Cu 90, Al 10	Hard, non-corrodible. Used in parts exposed to tanning, sulphite and simi- lar corrosive liquors.
Bearing	Sn 1-10 Pb 0-15 Zn 0-27	Bearings of various sorts.
Gear	Cu 89, Sn 11	Used for heavy gears usually against steel.
	Cu 88, Zn 10-8, Sn 2, Pb 2	Strong valves and fittings.
Phosphor		Bearing metal, wire, rods, steam fittings.
Plastic		Bearing metal.
Silicon	Cu 96, Sn 4, Si tr.	Telegraph wires, electrical work.
Babbitt metal	Sb 7-24	Bearings and antifriction lining for bronze bushings.
"Genuine"	Sn 88.9 Sb 7.4 Cu 3.5	

TABLE 3.—Continued

Name	Per cent. composition	Uses
Bell metal	Cu 80-75	Bells, gongs, etc.
	Sn 20–25	
	(Sometimes Ag, Ni	
Brass,	or other metals)	
Gilding metal	Cu 99-80	Cheap jewellery, gold paint
Guding metal	Zn 1–20	Chesp Jewenery, gold paint
Dutch metal	Cu 80–76	Thin sheets as substitute
Duven mevar	Zn 20-24	for gold leaf.
Standard		Brass for cold working
Domination	Zn 27-34	Sheets, tubes, cartridges.
White	Cu—less than 45	Ornamental castings not
		requiring strength.
Brazing metal	Cu 85-Zn 15	1
Britannia metal	Sn 95-90	Cheap table ware.
	Sb 5-10	_
	Cu 1-3	
Chromel	Ni 60	Resistance wire for heating
(Nichrome)	Cr 40	units, crucibles, triangles,
,	(approximate)	tongs. (Patented.)
Cupro-nickel	Cu 98-52	Projectile driving bands,
-	Ni 2–48	rifle bullet caps, electrical resistances.
Constantan	Cu 60	Used with copper or iron to
	Ni 40	make thermocouples.
Delta metal	Cu 60 ·	See Sterro metal.
	Zn 40	·
	Mn 0.5–2	
Duralumin	Al 95.5	Strongest and best of alumi-
	Cu 3.0	num alloys. Used in air-
	Mn 1.0	plane and automobile
	Mg 0.5	parts.
Fusible metals		
Lipowitz	Bi 50	These and other ternary and
	Pb 27	quaternary alloys are
	Sn 13	used for fuse plugs for
Was de	Cd 10 Bi 38	automatic sprinklers.
Woods	Bi 38 Pb 31	
	Pb 31 Sn 15	
	Sn 15 Cd 16	,
	Ou 10	

APPENDIX

TABLE 3.—Continued

Name	Per cent. composition	Uses
German silver		See nickel silver.
Gun metal	Cu 92–88	Gears, heavy hydraulic cast-
	Sn 8-12	ings.
		Same as aluminum brass
•	, Fe	with added toughness.
Invar	Fe 64	Low coefficient of expan-
	Ni 36	sion. Used in clocks, pre-
	1	cision instruments.
${\bf Magnalium}\dots\dots\dots$		Scientific instruments. Bal-
	Mg 10–6	ance beams.
Magnolia metal	Pb 78	Antifriction, bearing alloy.
(Lead base babbitt)		
	Sn 6	
Manganese bronze		Propeller blades. Non-
	Sn 10	corrodible and great wear-
	Mn 2	ing qualities.
Manganin		High electrical resistance
	Mn 15	and low temperature co-
	Ni 2.3	efficient.
Manal matal	Fe 0.6 Ni 72	Almost non-corrodible.
Monel metal	N1 72 Cu 26.5	Used for propeller blades,
	Fe 1.5	wire, sheets, etc.
Muntz metal		Sheathing for ships, bolts,
	Zn 40	nuts, condenser tubes.
Naval brass		Properties like Muntz
Mavai Diass	Zn 37	metal. Less easily cor-
	Sn 1.	roded by sea water.
Nickeliu		Resistance wire.
	Ni 25	
	Fe 0.5	
Nickel silver	Ni 18–25	Table ware, cheap jewellery,
(German silver)	Zn 20-30	base for silver plating.
(Cu (Remainder)	
Palau		Substitute for platinum in
	Au	chemical crucibles, dishes, etc. (Patented.)
Pewter	Sn 85-90	Platters, bowls, cups, etc.
	Sb 15-10	Little used at present.
Platinoid	Cu 60	High resistance wire but
	Zn 24	not suitable for heating
	Ni 14	coils.
	W 1-2	

TABLE 3.—Continued

Name .	Per cent. composition	Uses								
Platinite	Fe 54	Same coefficient of expan-								
,	Ni 46	sion as glass. Used as								
	C 0.15	substitute for platinum in equipping incandescent lamps.								
Platinum Iridium	Pt 90	Standard meter and other								
; }	Ir 10	standards. Thermo- couple with platinum.								
Rheotan	Cu 52	High resistance but not								
	Zn 18	suitable for heating coils.								
	Ni 25									
	Fe 5									
Shot metal	Pb 99	Casting bullets and small								
	As 1	shot.								
Solder		\(\)								
Soft	Pb 67, Sn 33	Plumbers solder.								
'Medium	Pb 50, Sn 50									
Hard	Pb 33, Sn 67									
Speculum metal	Cu 70–65 Sn 30–35	Takes a high polish. Formerly used in reflectors for telescopes.								
Steel		for telescopes.								
Plain Carbon	C 0.05-0.15	Boiler plate, rivets, sheet steel, case hardening stock.								
	C 0.15-0.25	Structural work bridges, shafting.								
	C 0.25-0.40	Axles, connecting rods, piston rods.								
	C 0.4-0.75	Rails, steel castings.								
	C 0.6-0.8	Cutlery, wood working tools, drills.								
1	C 0.8-1.0	Springs, lathe tools, drills.								
!	C 1.0-1.2	Large lathe tools, axes, knives.								
	C 1.2–1.5	Saws, files, balls for bearings, razors.								
Chrome	Cr less than 3	Projectiles, files.								
Chrome-tungsten		High speed tools. May be								
	W 5-25	run at 500°-600°C. without								
İ	Cr 2–10	losing their edge.								
ļ	Vd 0.25–1									

APPENDIX

TABLE 3.—Continued

Name	Per cent. composition	Uses
Steel (continued)		
Chrome-	C 0.25-1	Gears and springs.
vanadium	Cr 0.8-1.1	
	Vd 0.15	•
Manganese	Mn 6–15	Used on sharp railroad curves, frogs, switches, etc., where wear is hard.
Nickel	Ni 3–4	Drive shafts, crank shafts, gears and other automobile parts.
Nickel-	Ni 1-4	Armor plate
chromium	Cr 0.45-2	
Silicon	Si, less than 5	Has high permeability and low hysteresis. Used in dynamo construction.
Stellite	Co 80-50	Non-corrodible. Used in
	Cr 20-50	cutlery, surgical instru- ments. (Patented.)
Sterro metal	Cu 60	Strong as mild steel and not
(Aich's metal Delta	Zn 38	easily corroded. Used in
metal)	Fe 2	hydraulic cylinders, sea water valves.
Type metal	Pb 60-85	
	Sb 8-20	
•	Sn 5-35	

TABLE 4.

Temperature Conversion Table (Condensed)

Degrees Centigrade to Degrees Fahrenheit.

Degrees Fahrenheit = % Degrees Centigrade + 32°.

Degrees Centigrade = $\frac{5}{6}$ (Degrees Fahrenheit - 32°).

Degrees→ Centigrade	0	10	20	30	40	50	60	70	80	90
+	ı			Degree	Fahren	heit		•		
0	32	50	68	86	104	122	140	158	176	194
100	212	230	248	266	284	302	320	338	356	374
200	392	410	428	446	464	482	500	518	536	55-
300	572	590	608	626	644	662	680	698	716	73
400	752	770	788	806	824	842	860	878	896	914
500	932	950	968	986	1004	1022	1040	1058	1076	1094
600	1112	1130	1148	1166	1184	1202	1220	1238	1256	1274
700	1292	1310	1328	1346	1364	1382	1400	1418	1436	1454
800	1472	1490	1508	1526	1544	1562	1580	1598	1616	1634
900	1652	1670	1688	1706	1724	1742	1760	1778	1796	1814
1000	1832	1850	1868	1886	1904	1922	1940	1958	1976	1994
1100	2012	2030	2048	2066	2084	2102	2120	2138	2156	2174
1200	2192	2210	2228	2246	2264	2282	2300	2318	2336	2354
1300	2372	2390	2408	2426	2444	2462	2480	2498	2516	2534
1400	2552	2570	2588	2606	2624	2642	2660	2678	2696	2714
1500	2732	2750	2768	2786	2804	2822	2840	2858	2876	2894
1600	2912	2930	2948	2966	2984	3002	3020	3038	3056	3074
1700	3092	3110	3128	3146	3164	3182	3200	3218	3236	3254
1800	3272	3290	3308	3326	3344	3362	3380	3398	3416	3434
1900	3452	3470	3488	3506	3524	3542	3560	3578	3596	3614
2000	3632	3650	3668	3686	3704	3722	3740	3758	3776	3794

Table 5.

Melting Points and Atomic Weights of the More Important
Metals and Metalloids

Element	Symbol	Atomic weight	Melting point, deg. C.
Aluminum	Al	27.1	658.7
Antimony	Sb	120.2	630.5
Arsenic	As	75.0	850.0 (?)
Barium	Ba	137.4	850.0
Beryllium	Be	9.1	1278.0
Bismuth	Bi	208.0	271.0
Boron	В	11.0	2000.0-2500.0 (?)
Cadmium	Cd	112.4	320 .9
Calcium	Ca	40.1	800.0 ca.
Carbon	C(Diamond)	12.0	>3600.0
Cerium	Ce	140.25	> 800.0
Cæsium		132.9	26.0
Cobalt		59.0	1480.0
Chromium	Cr	52.1	1520.0
Copper	Cu	63.6	1084.1
Gallium	Ga	70.0	30.0
Gold	Au	197.2	1063.5
Indium	In	115.0	155.0
Iridium	Ir	193.0	2350.0 (?)
Iron	Fe	55.9	1530.0
Lanthanum	La	138.9	810.0 (?)
Lead	Pb	206.9	327.4
Lithium	Li	7.03	186.0
Magnesium	Mg	24.36	635.0
Manganese	Mn	55.0	1260.0
Mercury	Hg	200.0	-38.9
Molybdenum	Mo	96.0	2500.0 (?)
Nickel	Ni	58.7	1451.0
Osmium	Os	191.0	2700.0 (?)
Palladium	Pd	106.5	1549.0
Phosphorus	P	31.0	I.44-II.930
Platinum	Pt	194.8	1780.0
Potassium	K	39.15	62.5
Rubidium	$\mathbf{R}\mathbf{b}$	85.5	38.0
Ruthenium	Ru	101.7	2450.0(?)
Selenium	Se	79.2	217.0
Silicon	Si	28.4	1420.0
Silver	Ag	107.93	961.5
Sodium	Na	23.5	97.5

TABLE 5.—Continued

Element	Symbol	Atomic weight	Melting point, deg. C.						
Sulphur	s	32.6	I. 112.8-II. 119.2 III. 106.2						
Strontium	Sr	87.6	>Ca, $<$ Ba(?)						
Thallium	Tl	204.1	302.0						
Tellurium	Te	127.6	450.0						
Tin	Sn	119.0	232.0						
Titanium	Ti	48.1	1800.0						
Tungsten	w	184.0	>3000.0						
Uranium	Ur	238.5	<1850.0						
Vanadium	\mathbf{v}	51.2	1720.0						
Zinc	Zn	65.4	419.0						

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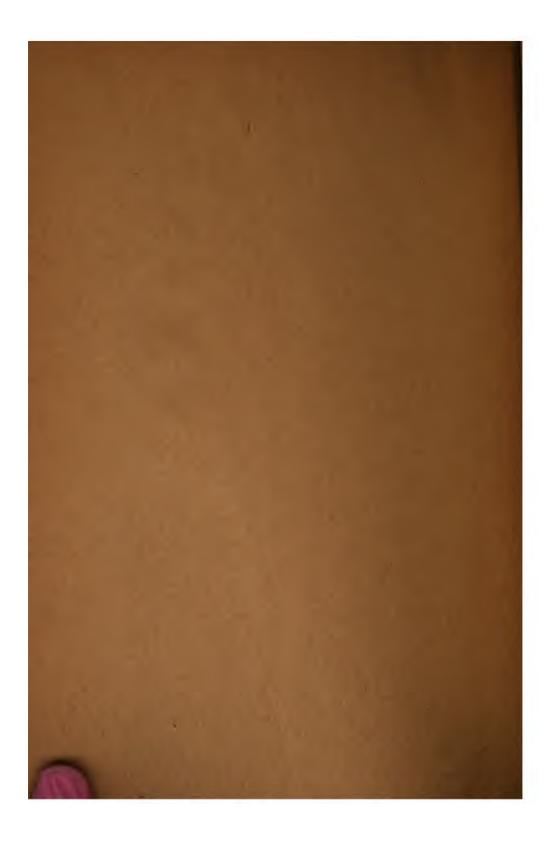
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